Densification of Selected Agricultural Crop Residues as Feedstock for the Biofuel Industry

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Phani Kumar Adapa

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Abstract

The two main sources of biomass for energy generation are purpose-grown energy crops and waste materials. Energy crops, such as Miscanthus and short rotation woody crops (coppice), are cultivated mainly for energy purposes and are associated with the food vs. fuels debate, which is concerned with whether land should be used for fuel rather than food production. The use of residues from agriculture, such as barley, canola, oat and wheat straw, for energy generation circumvents the food vs. fuel dilemma and adds value to existing crops. In fact, these residues represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass.

In order to reduce industry's operational cost as well as to meet the requirement of raw material for biofuel production, biomass must be processed and handled in an efficient manner. Due to its high moisture content, irregular shape and size, and low bulk density, biomass is very difficult to handle, transport, store, and utilize in its original form. Densification of biomass into durable compacts is an effective solution to these problems and it can reduce material waste. Upon densification, many agricultural biomass materials, especially those from straw and stover, result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture. This is caused by lack of complete understanding on the natural binding characteristics of the components that make up biomass.

An integrated approach to postharvest processing (chopping, grinding and steam explosion), and feasibility study on lab-scale and pilot scale densification of non-treated and steam exploded barley, canola, oat and wheat straw was successfully established to develop baseline data and correlations, that assisted in performing overall specific energy analysis. A new procedure was developed to rapidly characterize the lignocellulosic composition of agricultural biomass using the Fourier Transform Infrared (FTIR) spectroscopy. In addition, baseline knowledge was created to determine the physical and frictional properties of non-treated and steam exploded agricultural biomass grinds.

Particle size reduction of agricultural biomass was performed to increase the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the

compaction process. Predictive regression equations having higher R^2 values were developed that could be used by biorefineries to perform economic feasibility of establishing a processing plant. Specific energy required by a hammer mill to grind non-treated and steam exploded barley, canola, oat and wheat straw showed a negative power correlation with hammer mill screen sizes.

Rapid and cost effective quantification of lignocellulosic components (cellulose, hemicelluloses and lignin) of agricultural biomass (barley, canola, oat and wheat) is essential to determine the effect of various pre-treatments (such as steam explosion) on biomass used as feedstock for the biofuel industry. A novel procedure to quantitatively predict lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat straw was developed using Fourier Transformed Infrared (FTIR) spectroscopy. Regression equations having R^2 values of 0.89, 0.99 and 0.98 were developed to predict the cellulose, hemicelluloses and lignin compounds of biomass, respectively. The average absolute difference in predicted and measured cellulose, hemicellulose and lignin in agricultural biomass was 7.5%, 2.5%, and 3.8%, respectively.

Application of steam explosion pre-treatment on agricultural straw significantly altered the physical and frictional properties, which has direct significance on designing new and modifying existing bins, hoppers and feeders for handling and storage of straw for biofuel industry. As a result, regression equations were developed to enhance process efficiency by eliminating the need for experimental procedure while designing and manufacturing of new handling equipment.

Compaction of low bulk density agricultural biomass is a critical and desirable operation for sustainable and economic availability of feedstock for the biofuel industry. A comprehensive study of the compression characteristics (density of pellet and total specific energy required for compression) of ground non-treated and steam exploded barley, canola, oat and wheat straw obtained from three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm at 10% moisture content (wb) was conducted. Four preset pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were applied using an Instron testing machine to compress samples in a cylindrical die. It was determined that the applied pressure (60.4%) was the most significant factor affecting pellet density followed by the application of steam explosion pre-treatment (39.4%). Similarly, the type of biomass (47.1%) is the most significant factor affecting durability followed by the application of pre-treatment (38.2%) and grind size (14.6%). Also, the applied pressure (58.3%) was the most

significant factor affecting specific energy required to manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar effect affect on specific energy. In addition, correlations for pellet density and specific energy with applied pressure and hammer mill screen sizes having highest R^2 values were developed. Higher grind sizes and lower applied pressures resulted in higher relaxations (lower pellet densities) during storage of pellets.

Three compression models, namely: Jones model, Cooper-Eaton model, and Kawakita-Ludde model were considered to determine the pressure-volume and pressure-density relationship of non-treated and steam exploded straws. Kawakita-Ludde model provided the best fit to the experimental data having R^2 values of 0.99 for non-treated straw and 1.00 for steam exploded biomass samples. The steam exploded straw had higher porosity than non-treated straw. In addition, the steam exploded straw was easier to compress since it had lower yield strength or failure stress values compared to non-treated straw.

Pilot scale pelleting experiments were performed on non-treated, steam exploded and customized (adding steam exploded straw grinds in increments of 25% to non-treated straw) barley, canola, oat and wheat straw grinds obtained from 6.4, 3.2, 1.6 and 0.8 mm hammer mill screen sizes at 10% moisture content (wb). The pilot scale pellet mill produced pellets from ground non-treated straw at hammer mill screen sizes of 0.8 and 1.6 mm and customized samples having 25% steam exploded straw at 0.8 mm. It was observed that the pellet bulk density and particle density are positively correlated. The density and durability of agricultural straw pellets significantly increased with a decrease in hammer mill screen size from 1.6 mm to 0.8 mm. Interestingly, customization of agricultural straw by adding 25% of steam exploded straw by weight resulted in higher durability (> 80%) pellets but did not improve durability compared to non-treated straw pellets. In addition, durability of pellets was negatively correlated to pellet mill throughput and was positively correlated to specific energy consumption. Total specific energy required to form pellets increased with a decrease in hammer mill screen size from 1.6 to 0.8 mm and also the total specific energy significantly increased with customization of straw at 0.8 mm screen size. It has been determined that the net specific energy available for production of biofuel is a significant portion of original agricultural biomass energy (89-94%) for all agricultural biomass.

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Chapter 1

1. Introduction and Objectives

1.1 Introduction

In Canada, biomass energy accounts for 540 PJ (petajoules) of energy use accounting for 5% of secondary energy use by the residential sector and 17% of energy use in the industrial sector, mainly in the forest industries. It already provides more of Canada's energy supply than coal (for non-electrical generation applications) and nuclear power. The forestry sector (including lumber, pulp and paper) accounts for 35% of Canada's total energy consumption, however, they meet more than one-half of this demand themselves with self-generated biomass wastes (The Canadian Encyclopaedia, 2007).

The two main sources of biomass for energy generation are purpose-grown energy crops and waste materials (Larkin et al., 2004). Energy crops, such as Miscanthus and short rotation woody crops (coppice), are cultivated mainly for energy purposes and are associated with the food vs. fuels debate, which is concerned with whether land should be used for fuel rather than food production. The use of residues from agricultural production, such as barley, canola, oat and wheat straw, for energy generation circumvents the food vs. fuel dilemma and adds value to existing crops (Chico-Santamarta et al., 2009). In fact, these residues represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass (Liu et al., 2005).

Using agricultural crop residue available in Canadian Prairies has potential for the production of bio-fuels and offset greenhouse gas emissions. Canada has about 36.4 Mha of crop lands available for agricultural production. Out of that, more than 85% (about 32 Mha) are located on the Canadian Prairies (Alberta, Saskatchewan and Manitoba) and a small portion of northeast British Columbia (Campbell et al., 2002; Sokhansanj et al., 2006). After grain harvesting, most crop residues are left on the field. Some of these residues have been used for livestock feeding, bedding, insulation and mulching. Therefore, total surplus wheat, barley, oat and flax straw

available for bio-fuel production from prairies amounts to just over 15 Mt, with a wide annual variation from a maximum of 27.6 Mt to a low of 2.3 Mt. Some of the barriers to the economic use of agricultural crop residue are uncertainty in its availability, its quality, cost of collection, transport and storage, and its location (Bowyer and Stockmann, 2001; Sokhansanj et al., 2006).

The main problem with crop straw is its relatively low density in its original or baled forms. The bulk density of loose and standard baled straw is approximately 40 kg/m^3 and 100 kg/m^3, respectively, compared with the bulk density of unprocessed wood residue, which is approximately 250 kg/m^3 (Demirbas, 2001; Tripathi et al., 1998). The relative low density of straw makes it more expensive to transport compared to wood and coal because a lower mass of straw can be transported per unit volume. Additionally, a larger storage area/volume is required for baled straw compared to wood chip. Densification into pellets increases the bulk density of biomass (McMullen et al., 2005; Obernberger and Thek, 2004) and as a result, the net calorific content per unit volume is increased (Bhattacharya et al., 1989) and the storage, transport and handling of the material is easier and cheaper (Balatinecz, 1983; Bhattacharya et al., 1989; Kaliyan and Morey, 2006).

The quality of fuel pellet is usually assessed based on its density and durability. High bulk density increases storage and transport capacity of pellets (Adapa et al., 2007; Mani et al., 2003). Since feeding of boilers and gasifiers generally is volume-dependent, variations in bulk density should be avoided (Larsson et al., 2008). A bulk density of 650 kg/m^3 is stated as design value for wood pellet producers (Obernberger and Thek, 2004). Low durability of pellets results in problems like disturbance within pellet feeding systems, dust emissions, and an increased risk of fire and explosions during pellet handling and storage (Temmerman et al., 2006).

Densification of straw and determining the optimal parameters for processing into pellets is an art in itself. The entire process followed in this research involved securing of baled straw from agricultural fields, size reduction (chopping and grinding), application of pre-treatment (steam explosion), determining the physical and frictional properties of straw grinds, lignocellulosic characterization of straw, densification of grinds into pellets to determine the effect of various independent parameters on quality (density and durability), and energy analysis/ balance (Figure 1.1).

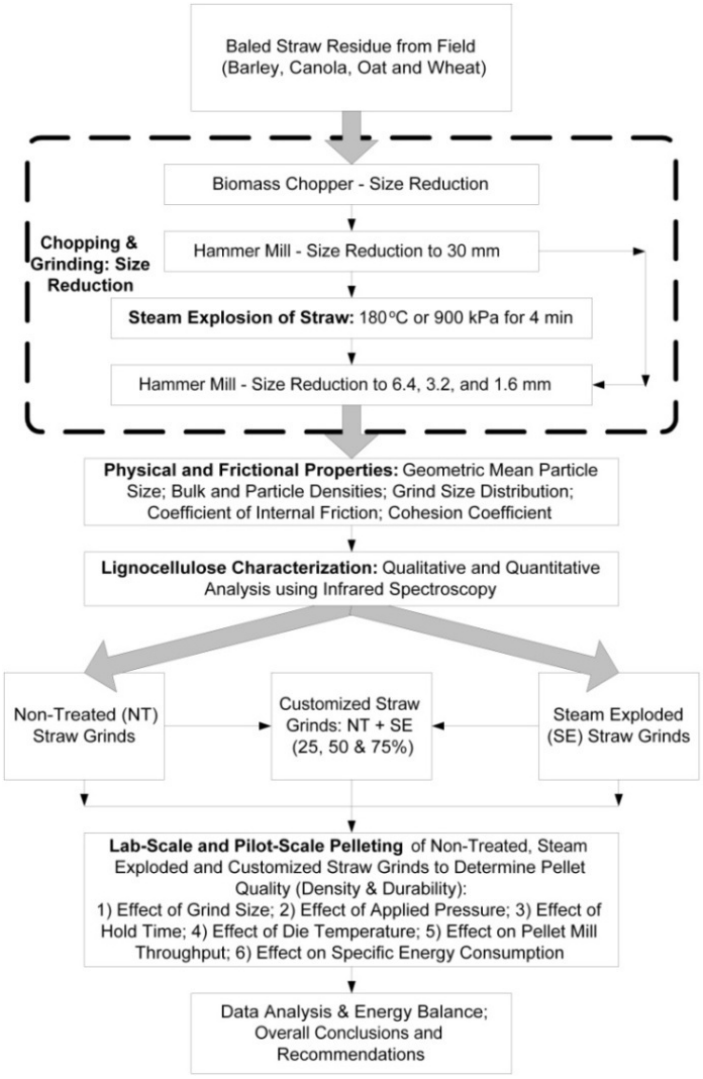


Figure 1.1: Processing steps involved in converting agricultural straw from field to pelletized product

It is critical to further analyze the post-harvest and processing steps indicated in Figure 1.1 since they have direct effect on the quality of pellets manufactured. The following sections (1.2 to 1.6) will highlight the need for these steps and their effect on pellet quality, which will form the basis of the thesis objectives.

1.2 Steam Explosion Pre-treatment

Upon densification, many agricultural biomass, especially those from straw and stover, result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to

manufacture. This is caused by lack of complete understanding of the natural binding characteristics of the components that make up biomass (Sokhansanj et al., 2005). The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). It is postulated that by disrupting the lignocellulosic matrix of biomass materials via steam explosion pretreatment, the compression and compaction characteristics can be improved (Shaw, 2008). When high molecular amorphous polysaccharides are reduced to low molecular components, the polymer becomes more cohesive in the presence of moisture (Chen et al., 2004). The cellulose-hemicellulose-lignin matrix can be broken down to smaller amorphous molecules through acid or alkaline hydrolysis as well as through steam explosion (Ladisch, 1989; Vlasenko, 1997). Alkaline or acid solutions are often used for pre-treatment of biomass and the effect of pre-treatment depends on the lignin content of biomass. When biomass is treated with dilute alkaline solution, the internal surface area of the material is increased by swelling. Swelling causes a decrease in the degree of polymerization, separation of structural linkages between lignin and carbohydrates and disruption of the lignin structure (Fan et al., 1987). Increased moisture content resulting from chemical and enzymatic treatments is a problem, as the treated biomass has to be dried prior to densification. Steam explosion results in the hemicelluloses being hydrolyzed and water soluble, the cellulose is slightly depolymerized, the lignin melts and is depolymerized, which aid in binding particles together during densification. Zandersons et al. (2004) stated that activation of lignin and changes in the cellulosic structure during the steam explosion process facilitate the formation of new chemical bonds. Lam et al. (2008) reported that the quality (durability) of compacts produced from steam exploded sawdust was 20% higher than non-treated sawdust.

Steam explosion is one of the most applied pre-treatment processes owing to its low use of chemicals and limited energy consumption (Harmsen et al., 2010). During steam explosion pre-treatment process, the lignocellulosic biomass is heated with high pressure saturated steam having temperatures typically in the range of 180-230^{o}C for 2-10 minutes. Subsequently, the substrate is quickly flashed to atmospheric pressure; as a result, the water inside the substrate vaporizes and expands rapidly, disintegrating the biomass (Grous et al., 1985; Kokta and Ahmed, 1998; Zimbardi et al., 1999). This causes great reduction in the particle size of the substrate and also increases the availability of free lignin, which is not bound within the lignocellulosic matrix.

1.3 Particle Size Reduction

The application of pretreatment operations such as size reduction / grinding is critical in order to increase the surface area of the material prior to densification (Mani et al., 2004). Particle size reduction increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process (Drzymala, 1993). Size reduction is an important energy intensive unit operation essential for bioenergy conversion process and densification to reduce transportation costs (Bitra et al., 2009; Soucek et al., 2003). Energy consumption of grinding biomass depends on initial particle size, moisture content, material properties, feed rate of the material and machine variables (Bitra et al., 2009; Lopo, 2002).

Chopping / Tub Grinding: Baled agricultural biomass from the field does not have good flowing characteristics and may not flow easily into grinders such as hammer mills and disc refiners. Therefore, biomass needs to be chopped with a chopper (rotary shear shredder) / knife mill / tub grinder to accommodate bulk flow and uniformity of feed rate. A chopper, knife cutter, or knife mill is often used for coarse size reduction (>50 mm) of stalk, straw, and grass feed stocks (Bitra et al., 2009). Knife mills reportedly worked successfully for shredding forages under various crop and machine conditions (Cadoche and López, 1989).

Bitra et al. (2009) reported that the total specific energy (including energy to operate the knife mill) for agricultural biomass chopping increases with knife mill speed. The total specific energy for knife mill and tub grinder has been observed to have negative correlation with screen size and mass feed rate (Arthur et al., 1982; Bitra et al., 2009; Himmel et al., 1985). However, grinding rate (throughput) increases with an increase in screen size (Arthur et al., 1982).

For tub grinders, an increase in screen size results in an increase in geometric mean length of particles and throughput, but a decrease in bulk density of the particles and specific energy consumption (Kaliyan et al., 2010).

Hammer Mills: Typically, hammer mills are used in forage processing industry as they are relatively inexpensive, easy to operate and produces wide range of particles (Lopo, 2002). Hammer mills have achieved merit because of their ability to finely grind a greater variety of materials than any other machines (Scholten et al., 1985). The performance of a hammer mill is

measured in terms of energy consumption and geometric mean diameter and particle size distribution of the ground product (Mani et al., 2004).

Screen Size: Hammer mill screen opening size was the most significant factor affecting mill performance (Fang et al., 1997) and also has significant effect on mean particle size (Pfost and Headley, 1971). The specific energy required to grind agricultural biomass significantly increases with a decrease in hammer mill screen size and shows a negative power correlation (Arthur et al., 1982; Soucek et al., 2003). Two other studies reported a second-order polynomial relationship between the specific energy requirements for grinding biomass (Mani et al. 2004; Sitkei, 1986). Usually, the mean geometric particle size for any particular biomass decreases with a decrease in hammer mill screen size. It has been reported that wider particle size distribution is suitable for compaction (pelleting/ briquetting) process (Mani et al., 2004). During compaction, smaller (fine) particles rearrange and fill in the void space of larger (coarse) particles producing denser and durable compacts (Tabil, 1996).

Operating Speed (Peripheral Velocity): The speed has a significant effect on mean particle size (Pfost and Headley, 1971). The total specific energy of hammer mill grinding has direct correlation to an increase in hammer tip speed (Bitra et al., 2009; Vigneault et al., 1992). High speed hammer mills with smaller diameter rotors are good for fine or hard-to-grind material. However, at high tip speeds, material moves around the mill parallel to the screen surface making the openings only partially effective. At slower speeds, the material impinges on the screen at a greater angle causing greater amounts of coarser feed to pass through (Balk, 1964).

Hammer Angles and Thickness: The direct energy input for grinding also depends on hammer angles. In general, the specific energy for grinding decreases with an increase in hammer degrees (Bitra et al., 2009). In addition, the specific energy for grinding increases with an increase in hammer thickness (Vigneault et al., 1992).

Material Moisture Content and Feed Rate: A positive correlation has been reported between moisture content and specific energy consumption for grinding of agricultural biomass (Balk, 1964; Mani et al., 2004; Soucek et al., 2003). Feeding rate also has significant effect on specific energy consumption during hammer mill grinding and has positive correlation (O'Dogherty, 1982).

Bulk and Particle Densities, and Geometric Mean Particle Size: Usually, the bulk and particle density of agricultural straw significantly increases with a decrease in hammer mill screen size. The geometric mean particle size of pre-treated straw is usually smaller than that of the non-treated straw. This could be due to the fact that application of pre-treatment disrupts/ disintegrates the lignocellulosic structure of the biomass (Sokhansanj et al., 2005) leading to lower shear strength (easier to grind the straw).

1.4 Physical and Frictional Properties

Prior to densification, biomass grinds need to be efficiently stored, handled and transported. Physical and frictional properties of biomass have significant effect on design of new and modification of existing bins, hoppers and feeders (Fasina et al., 2006). The frictional behavior of biomass grinds in all engineering applications is described by two independent parameters: the coefficient of internal friction, and the coefficient of wall friction. The former determines the stress distribution within particles undergoing strain, and the latter describes the magnitude of the stresses between the particle and the walls of its container (Seville et al., 1997). The classic law of friction states that frictional force is directly proportional to the total force that acts normal to the shear surfaces (Larsson, 2010). Frictional force depends on the nature of the materials in contact but is independent of the area of contact or sliding velocity (Mohsenin, 1970). Material properties such as moisture content and particle size affect the frictional properties and densification performance of an individual feedstock (Larsson, 2010; Shaw and Tabil, 2006). In addition, the determination of coefficient of friction is essential for the design of production and handling equipment and in storage structures (Puchalski and Brusewitz, 1996).

1.5 Rapid Determination of Lignocellulosic Biomass Composition

The effect of various pre-processing and pre-treatment methods on the lignocellulosic matrix at the molecular level is not well understood. Applications of pre-processing methods such as size reduction or increasing porosity, and pre-treatment techniques such as steam explosion on agricultural biomass have demonstrated an improvement in pellet (compact) quality that can be attributed to the changes in the lignocellulosic components and distribution (Bagby, 1982; Focher et al., 1998). Therefore, it is critical to rapidly quantify the change in cellulose, hemicelluloses and lignin components of biomass due to application of pre-treatment methods.

Infrared spectroscopy has the potential to produce qualitative and quantitative analytical data for samples with minimum or no sample preparation, and at high speed and throughput (Budevska, 2002; Luypaert et al., 2003; Smola and Urleb, 2000; Tucker et al., 2000). Traditionally, chemical analyses of the individual components (e.g., lignin) of lignocellulosics have been performed by acid hydrolysis followed by gravimetric determination of lignin (Kelley et al., 2004). These methods can provide highly precise data. However, these methods are laborious, time-consuming, and, consequently, expensive to perform and sample throughput is limited. Hence, there is a need to develop analytical tools that can be used to rapidly and inexpensively measure the chemical composition of biomass (Gelbrich et al., 2009; Kelley et al., 2004; Vazquez et al., 2002).

1.6 Lab-Scale and Pilot-Scale Pelleting

A compression apparatus having a close fit plunger die assembly can be used to make a single compact in one stroke of the plunger from ground straw samples (Adapa et al., 2006; Mani et al., 2004). The compression test should be performed to study the effect of independent variables such as biomass, treatment, grind size, and moisture content on pellet density and durability. In order to simulate frictional heating during commercial pelleting operation, the compression die should be maintained at pre-heat temperatures of 75 to 100^{o}C (Adapa et al., 2006; Kaliyan and Morey, 2009; Mani et al., 2006). Different levels of pre-set compressive forces can be applied using the Instron testing machine. Typical pre-set loads in the range of 31.0 to 150.0 MPa are applied to make pellets. During the compression and extrusion processes of individual biomass compacts, the force-displacement data is recorded and can be used to calculate the specific compression and extrusion energies following the methodology reported by Adapa et al. (2006) and Mani et al. (2006).

The compression characteristics of ground agricultural biomass vary under various applied pressures. It is important to understand the fundamental mechanism of the biomass compression process, which is required to design an energy efficient compaction equipment to mitigate the cost of production and enhance the quality of the product (Mani et al., 2004). To a great extent, the strength of manufactured compacts depends on the physical forces that bond the particles together (Tabil and Sokhansanj, 1996). These physical forces are generated in three different

forms during compaction operations: a) thermal; b) mechanical; and c) atomic forces (Adapa et al., 2002). To customize and manufacture high quality products that can withstand various forces during transportation and handling, it is essential to predict desirable and dependent quality parameters (density and durability) with respect to various independent variables (grind size, applied pressure, hold time, die temperature, and moisture content) (Adapa et al., 2007). In addition, specific energy requirements of manufacturing biomass pellets should be established, which can assist in determining the economic viability of densification process.

Pilot-scale densification of biomass is required to demonstrate the feasibility of production of pellets by application of various variables studied during single-pellet experiments. A pilot-scale pellet mill such as CPM CL-5 pellet mill (California Pellet Mill Co., Crawfordsville, IN) (Adapa et al., 2004) can be used for processing of agricultural straw grinds into pellets. The pellet mill usually consists of a corrugated roller and ring die assembly, which compacts and extrudes the biomass grinds from the inside of a ring-shaped die by pressure applied by rolls where either the die or the roll suspension is rotating. Rolls are mounted close to the die surface, but still leaving room for a compacted feed layer to enter the roll gap. Friction between feed layer and rolls makes the rolls rotate (Larsson et al., 2008). In addition to variables indicated in the single-pellet testing, the quality of pellets also depends on machine variables such as the ring die size (radius), length (thickness, l), ring hole diameter (*d*), *l/d* ratio, and the rotational speed of the pellet mill (Adapa et al., 2004; Hill and Pulkinen, 1988; Tabil and Sokhansanj, 1996). A monitoring study of commercial pellets was done by Hill and Pulkinen (1988), on variables such as die geometry, conditioning temperatures, natural moisture of the grind, forage quality, bulk density of the grinds, and the use of binding agents. Similarly, Larsson et al. (2008) studied the effect of raw material moisture content, steam addition, raw material bulk density, and die temperature on production of high quality pellets. Also, Serrano et al. (2011), determined the effect of grind size, moisture content and customization of barley straw by adding pine dust to the mixture (blended pellets). The feed rate of ground biomass to the pellet mill should be optimized according to the pellet mill capacity, which will directly affect the throughput. The pilot-scale pelleting test should be performed for a predefined period and the manufactured pellets should be collected and weighed to determine the pellet mill throughput (kg/h). In addition, the pellet mill energy consumption (kWh) should be recorded in real time using a data logger connected to a computer

and should be used to calculate the specific energy (MJ/t) required to manufacture pellets from ground agricultural biomass.

1.7 Objectives of Research

An integrated approach (Figure 1.1) to densification of non-treated and steam exploded barley, canola, oat and wheat straw has never been reported in the literature. In addition, to determine the feasibility of densification of agricultural straw and investigate the effect of various independent variables such as grind size, applied pressure, hold time, die temperature, and moisture content on density and durability of pellets, it is critical to develop a process with various options and subsequently establish optimal conditions. Therefore, the objectives of the present study were:

1. to determine and establish relationships of geometric mean particle size with specific energy requirements, bulk and particle densities, and perform a comparative analysis for grinding non-treated and steam exploded barley, canola, oat and wheat straws;

2. to determine the effect of steam explosion pretreatment, hammer mill screen size, and normal forces on coefficient of internal friction and cohesion properties of non-treated and steam exploded barley, canola, oat and wheat straw;

3. to estimate critical parameters in analytical specification of lignocellulosic biomass and consequently, to develop and validate a rapid method for the qualitative and quantitative analysis of cellulose-hemicellulose-lignin composition of non-treated and steam exploded barley, canola, oat and wheat straw using Fourier Transform Infrared Spectroscopy (FTIR);

4. to determine the effect of pressure and biomass grind size on density and specific energy requirements for compacting non-treated and steam exploded barley, canola, oat and wheat straw grinds;

5. to determine the pressure-volume and pressure-density relationship to analyze the compression characteristics of non-treated and steam exploded barley, canola, oat and

wheat straw using three compression models, namely: Jones (1960), Cooper-Eaton (1962), and Kawakita-Ludde (1971), models;

6. to produce high density and high durability pellets from ground non-treated and steam exploded barley, canola, oat and wheat straw using a pilot-scale pellet mill; and

7. to perform an overall energy analysis of the entire postharvest and densification process.

1.8 Organization of the Thesis

The thesis is organized according to the University of Saskatchewan guidelines for manuscript-based theses. The information, experimental data and analysis reported in this thesis have already been published or in-press with peer-reviewed journals. The entire thesis has been divided into six projects, and manuscripts were written and published as each stage of Ph.D. project was completed. The manuscripts presented in Chapters 2, 3, 4, 5 and 6 have been published (or in-press) in peer-reviewed journals. The manuscript in Chapter 7, which is on overall energy analysis of the integrated densification process has been accepted as a conference proceeding paper and will be presented during the conference in July 2011. In each manuscript based-chapter, the contribution of the Ph.D. candidate and the contribution of the paper to the overall study are discussed in addition to the manuscript itself. Chapters 1, 8 and 9 are original text in this thesis included to introduce the subject matter and discuss the outcome of the project. The references provided in Chapters 1 to 8 are provided in Chapter 10.

1.9 Manuscript Content of the Thesis

The current Ph.D. research program has resulted in both generation of new knowledge and development of new procedures for testing and manufacturing of agricultural straw pellets. An integrated approach to agricultural biomass densification was adopted and presented in various chapters. In Chapter 2, experiments on particle size reduction of biomass was performed using a chopper and a hammer mill to determine and establish relationships of geometric mean particle size with specific energy requirements, bulk and particle densities, and perform a comparative analysis for grinding non-treated and steam exploded barley, canola, oat and wheat straws. Pellet mill operators and equipment designers can use this data to design a pilot scale chopping and grinding operation. The ground biomass obtained during the study conducted in Chapter 2

was used to develop baseline data and correlations in Chapter 3 to predict coefficient of internal friction, and cohesion coefficient with respect to the geometric mean particle size of non-treated and steam exploded barley, canola, oat and wheat straw grinds. The frictional properties of agricultural biomass can be used by manufacturers to design new and modify existing bins, hoppers and feeders for handling and storage of straw for biofuel industry. In Chapter 4, a review of the structural and chemical characteristics of agricultural biomass was successfully performed, which explored the basic concepts of infrared spectroscopy, and evaluated its strengths and drawbacks as applied to lignocellulosic biomass. In addition, a procedure to rapidly quantify the lignocellulosic composition of non-treated and steam exploded barley, canola, oat and wheat straw, which could be easily extended for any form of lignocellulosic biomass using FTIR spectroscopy was successfully developed. The material obtained from Chapter 2 was used in Chapter 5 to study the compression and compaction behavior of agricultural biomass grinds, which resulted in development of baseline data and correlations for pellet density and specific energy required for pelleting, with applied pressure and hammer mill screen size for both non-treated and steam exploded straw grinds. A relative comparison of non-treated and steam exploded agricultural biomass was performed that could be used by the biofuel pellet manufacturers to optimize various variables during the pelleting process. In Chapter 6, a procedure for pilot-scale pelleting of non-treated and steam exploded was successfully developed and practical problems related to flowability of grinds through pellet mill and production of high quality pellets were identified. Customization of straw was explored to enhance the natural binding capability of straw resulting in high density and durability pellets. Pilot-scale energy requirement was established, which is more practical for energy calculations and design of large-scale biofuel pelleting operations. Finally, an overall energy analysis was performed in Chapter 7 to determine whether there is a significant positive energy balance to the densification process enabling non-treated and steam exploded straw as suitable feedstock for biorefineries.

Chapter 2

2. Grinding Performance and Physical Properties of Non-Treated and Steam Exploded Barley, Canola, Oat and Wheat Straw

A similar version of this chapter has been published and presented in the journal of biomass and bioenergy, and at the ASABE/CSBE North Central Intersectional Conference, respectively:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2011. Grinding performance and physical properties of non-treated and steam exploded barley, canola, oat and wheat straw. *Biomass and Bioenergy*, 35(2011): 549-561.
- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2009. Grinding characteristics of selected non-treated and steam exploded agricultural biomass. ASABE/CSBE North Central Intersectional Conference, Student Union, South Dakota State University, Brookings, Paper No. SD09-600, September 18-19. St. Joseph, MI: ASABE.

Contributions of Ph.D. Candidate

The present study resulted in development of baseline data and correlations that could be used to predict bulk density and particle density of grinds, and specific energy required to grind non-treated and steam exploded barley, canola, oat and wheat straw with respect to geometric mean particle diameter of the grinds. Pellet mill operators and equipment designers can use this data to design a pilot scale chopping and grinding operation. All of the experiments, data analysis and

manuscript writing were performed by Phani Adapa with technical assistance of Mr. Anthony Opoku (Professional Research Associate), while Dr. Lope Tabil and Dr. Greg Schoenau provided editorial input. In addition, Dr. Lope Tabil established research collaboration with FPInnovations in Quebec City, Quebec to perform steam explosion treatment of agricultural biomass.

Contribution of this Paper to Overall Study

Knowledge Gap: It has been widely accepted that energy consumption of grinding biomass depends on initial particle size, moisture content, material properties, feed rate of the material and machine variables. Earlier work has been conducted on grinding of non-treated barley, oat and wheat straw. However, the research on grinding and mechanical properties of non-treated canola straw and steam exploded agricultural biomass is very scarce. Therefore, the present study was conducted with the objective to determine and establish relationships of geometric mean particle size with specific energy requirements, bulk and particle densities, and perform a comparative analysis for grinding non-treated and steam exploded barley, canola, oat and wheat straws.

Justification: Upon densification, many agricultural biomass materials, especially those from straw and stover, result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture. This is caused by lack of complete understanding on the natural binding characteristics of the components that make up biomass (Sokhansanj et al., 2005). Application of pre-treatment such as steam explosion and perform size reduction is essential in order to enhance the natural binding characteristics of agricultural biomass leading towards production of his quality (density and durability) pellets. The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). It is postulated that by disrupting the lignocellulosic matrix of biomass materials via application of steam explosion pre-treatment, the compression and compaction characteristics can be improved (Shaw 2008).

The application of pre-processing operations such as particle size reduction / grinding is critical in order to increase the surface area of lignocellulosic biomass prior to densification (Mani et al. 2004). Particle size reduction increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process (Drzymala, 1993). Size reduction is an important energy intensive unit operation essential for bioenergy conversion process and densification to reduce transportation costs (Bitra et al., 2009; Soucek et al., 2003).

2.1 Abstract

Grinding experiments were conducted on non-treated and steam exploded barley, canola, oat and wheat straw using a forage chopper and a hammer mill (screen sizes of 30, 6.4, 3.2 and 1.6 mm) to determine specific energy requirements, and geometric mean particle size and distribution of ground material. The bulk density of non-treated biomass was significantly higher than bulk density of steam exploded agricultural biomass. For non-treated agricultural straw, the particle density of canola and oat straw significantly increased with a decrease in hammer mill screen size from 30 to 1.6 mm. The particle density of steam exploded barley and oat straw was significantly higher than non-treated straw, except for barley at 6.4 mm hammer mill screen size. The particle density of steam exploded canola straw was not statistically different from non-treated straw. The chopper consumed highest (3.15±0.09 kWh t^{-1}) and lowest (1.96±0.33 kWh t^{-1}) specific energy to chop barley and canola straw, respectively. The highest and lowest specific energy was consumed by wheat (42.57±2.04 kWh t^{-1}) at 1.6 mm and canola (1.46±0.30 kWh t^{-1}) straws ground using 30 mm hammer mill screen size, respectively. For steam exploded agricultural biomass, the highest and lowest specific energy was consumed by oat (33.18±3.10 kWh t^{-1}) at 1.6 mm and canola (2.69±0.26 kWh t^{-1}) straws ground using 6.4 mm hammer mill screen size, respectively. Specific energy required by hammer mill to grind non-treated and steam exploded barley, canola, oat and wheat straw showed a negative power correlation with hammer mill screen sizes.

2.2 Introduction

Agricultural biomass residues such as barley, canola, oat and wheat straw are potential feedstocks for the sustainable production of bio-fuels and to offset greenhouse gas emissions (Campbell et al., 2002; Sokhansanj et al., 2006). The straw and agricultural residues from commercial crop processing plants have little inherent value and have traditionally constituted a disposal problem. In fact, these residues represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass (Liu et al., 2005).

Densification of biomass into durable pellets or briquettes is an effective solution to these problems and can reduce material waste. Densification can increase the bulk density of biomass from an initial bulk density of 40-200 kg m^{-3} to a final compact density of 600-1200 kg m^{-3} (Adapa et al., 2007; Holley 1983; Mani et al., 2003; McMullen et al., 2005; Obernberger and Thek, 2004) and a bulk density of 650 kg m^{-3} (Obernberger and Thek, 2004). Because of uniform shape and sizes, densified products can be easily handled using the standard handling and storage equipment, and can be easily adopted in direct combustion or co-firing with coal, gasification, pyrolysis, and in other biomass-based conversions (Kaliyan and Morey, 2006). Upon densification, many agricultural biomass materials, especially those from straw result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture (Sokhansanj et al., 2005). This is a result of lack of complete understanding on the natural binding characteristics of the components that make up biomass (Sokhansanj et al., 2005).

The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). It is postulated that by disrupting lignocellulosic biomass materials via steam explosion pretreatment, the compression and compaction characteristics can be improved (Shaw, 2008). The activation of lignin and changes in the cellulosic structure during the steam explosion process facilitate the formation of new bonds (Zandersons et al., 2004). Much of the research involving steam explosion pretreatment has focused on the alteration of the lignocellulose matrix in biomass, and subsequent improvement of enzymatic hydrolysis (Ballesteros et al., 2002; Nunes and Pourquie, 1996). Steam explosion has

also been explored by the flax fiber industry as an upgrading step to produce high quality short fibers for the textile market (Kessler et al., 1998). It has been reported that the quality (durability) of pellets produced from steam exploded sawdust was 20% higher than non-treated sawdust (Lam et al., 2008).

Densification of straw and determining optimal parameters is an art in itself. The entire process involves securing of baled straw from agricultural fields, size reduction (chopping and grinding), lab-scale and pilot-scale densification of grinds into pellets to determine the effect of various independent parameters on quality (density and durability), and energy analysis/ balance (Figure 1.1). The present paper is primarily focused on the "Chopping and Grinding" section of Figure 1.1 providing information on the importance of grinding.

Application of pretreatment such as size reduction/ grinding is a critical process in order to increase the surface area of the material prior to densification (Mani et al., 2004). Particle size reduction increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process (Drzymala, 1993). Typically, hammer mills are used in forage processing industry as they are relatively inexpensive, easy to operate and produces wide range of particles (Lopo, 2002). Hammer mills have achieved merit because of their ability to finely grind a greater variety of materials than any other machines (Scholten and McEllhiney, 1985).

Size reduction is an important energy intensive unit operation essential for bioenergy conversion process and densification to reduce transportation costs (Bitra et al., 2009; Soucek et al., 2003). Energy consumption of grinding biomass depends on initial particle size, moisture content, material properties, feed rate of the material and machine variables. The performance of a hammer mill is measured in terms of energy consumption and geometric mean diameter and particle size distribution of the ground product (Mani et al., 2004). The specific energy requirements of a hammer mill for different moisture content and feed rate for grinding coastal Bermuda grass was also studied (Balk, 1964). A study was conducted to measure the specific energy requirements of a hammer mill used to grind wheat straw, corn residues and grain sorghum residues at a peripheral speed of 15.8 m s^{-1} (Von Bargen et al., 1981). They have determined that the corn residue and grain sorghum residue consumed the highest and lowest

specific energy, respectively. Grinding experiments using hammer mill on corn and grain sorghum residue was also done elsewhere (Martin and Behnke, 1984). They have found that high power was consumed for fine grinding of material. Another study observed that total specific energy for size reduction of wheat straw using 1.6 mm hammer mill screen size was twice that for a 3.2 mm screen (Himmel et al., 1985). Hammer mill screen opening size was the most significant factor affecting mill performance (Fang et al., 1997) and also has significant effect on mean particle size (Pfost and Headley, 1971). A specific energy of 44.9 kWh t^{-1} was consumed when a hammer mill with screen size of 5.6 mm was used to grind switchgrass (Samson et al., 2008). Grinding experiments using hammer mill were conducted on wheat and barley straw, corn stover and switchgrass at two moisture levels and three grind sizes (Mani et al., 2004). The study concluded that among the four materials, switchgrass had the highest specific energy consumption of 27.6 kWh t^{-1}, and corn stover had the lowest specific energy consumption of 11.0 kWh t^{-1} at 3.2 mm screen size (Mani et al., 2004).

Another study observed that the specific energy consumption was increased by disintegration with reduction of output particles average length (sieve screen size of 1 mm) and an increase in moisture content of various forest residue and agricultural straw (Balk, 1964). In general, at moisture content higher than 12%, the specific energy consumption for small sieve screen size was inadequately high. The study also observed that during grinding by fine sieve screen size for a decrease in moisture content from 19.6 to 9.2% the specific energy consumption of grinding was reduced from 232.0 to 53.0 kWh t^{-1}. For larger sieve screen size (above 5 mm) the energy consumption of disintegration was comparable.

The direct energy inputs for grinding switchgrass, wheat straw, and corn stover using a hammer mill operating speeds of 33.3 to 60 Hz for 3.2 mm screen size and mass input rate of 2.5 kg min^{-1} with 90^{o}- and 30^{o}-hammers was also determined (Bitra et al., 2009). The study found that the total specific energy for switchgrass, wheat straw, and corn stover grinding increased by 37, 30, and 45% from 31.8, 34.8 and 28.8 kWh t^{-1}, respectively. In addition, the effective specific energy of 90^{o}-hammers decreased marginally for switchgrass and considerably for wheat straw and it increased for corn stover with an increase in speed from 33 to 60 Hz. However, the effective specific energy increased with speed to a certain extent and then decreased for 30^{o}-hammers. In general, the specific energy decreased with an increase in hammer degrees and

with an increase in speed. Another study observed a 13.6% saving in total specific energy requirement and an increase of 11.1% in grinding rate by using thin hammers (3.2 mm thickness) instead of thick hammers (6.4 mm thickness) without affecting geometric mean diameter and geometric standard deviation of corn grind (Vigneault et al., 1992). The total specific energy of hammer mill grinding of corn was increased from 4.7 to 12.8 kWh t^{-1} for an increase in hammer tip speed from 54 to 86 m s^{-1} for 6.4 mm-thick hammer (Bitra et al., 2009).

In the present study, grinding experiments on non-treated and steam exploded agricultural straw material (barley, canola, oat and wheat straw) were conducted to determine specific energy requirements, and geometric mean particle size and distribution. Earlier work has been reported on mechanical properties of ground barley and wheat straw (Mani et al., 2004), and on ground wheat straw as a feedstock for biofuel industry (Bitra et al., 2009). In addition, an empirical equation to determine specific energy required for grinding oat straw was also reported (Soucek et al., 2003). It has been widely accepted that energy consumption of grinding biomass depends on initial particle size, moisture content, material properties, feed rate of the material and machine variables. Therefore, it is essential to conduct grinding experiments and determine mechanical properties of proposed materials in this study as they will have direct effect on compact (pellet/briquette) quality. The available literature on grinding and mechanical properties of non-treated canola straw and steam exploded agricultural biomass is very scarce. Thus, the present study was conducted with the objective to determine and establish relationships of geometric mean particle size with specific energy requirements, bulk and particle densities, and perform a comparative analysis for grinding non-treated and steam exploded barley, canola, oat and wheat straws.

2.3 Materials and Methods

2.3.1 Size Reduction of Agricultural Biomass

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for the experiments. The straw samples were acquired from a farmer in the Central Butte area of Saskatchewan, Canada, from crops combined in August 2008 and left on the field to dry.

Subsequently, the straw was square baled in September 2008 (typically having dimensions of 0.45 x 0.35 x 1.00 m).

The initial moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (wb), respectively. The agricultural biomass was placed over a thick plastic sheet and left under a tarpaulin cover during the winter of 2008 (approximately for 7 months). During this period the moisture content of barley, canola, oat and wheat straw increased to 13.5, 15.1, 13.1 and 15.6% (wb), respectively.

All of the baled straw samples were chopped using a chopper, which was fabricated in the Bioprocessing Lab, Department of Agricultural and Bioresource Engineering, University of Saskatchewan (Fig. 2.1). The biomass chopper is a modified and compact version of the currently available New Holland Forage Chopper series 770 having similar specification of the chopper and cutter-bar, and motor size of 770 W. The biomass chopper was equipped with a feed hopper and a pair of rollers to feed the material to the chopping blades. The feed rate of biomass to the blades was dependent on the roller speed. After a few preliminary trials, the rollers were set to rotate at 0.83 Hz in order to avoid material clogging. Each of the six chopper blades were inclined at an angle of 14^{o} (with respect to horizontal axis of rotation) to deliver shearing effect on the biomass and were set to rotate at 7.7 Hz.

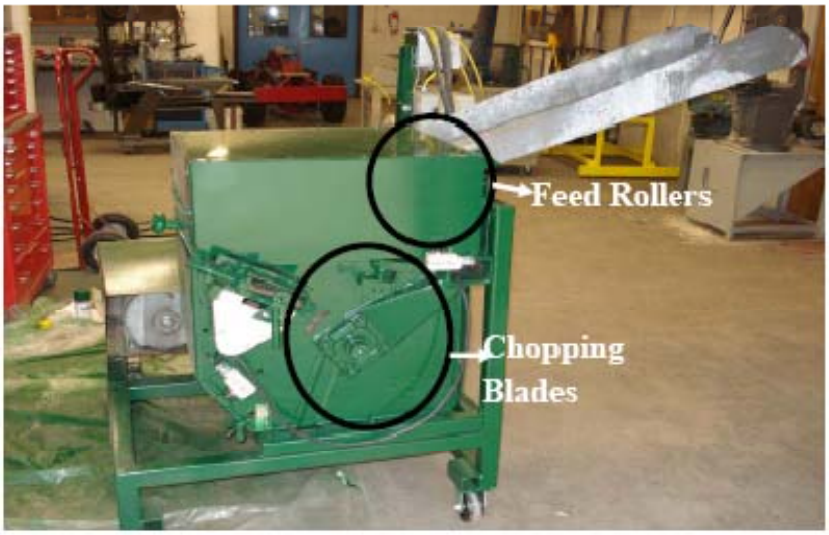
The chopped biomass was subsequently ground using a hammer mill (Serial no. 6M13688; 230 Brookdale, St. Maywood, NJ) having 22 swinging hammers, attached to a shaft powered by a 1.5 kW electric motor. The shaft rotated at 63.3 Hz. Four screen sizes of 30, 6.4, 3.2 and 1.6 mm were used to grind the non-treated biomass. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK) having a 9 A suction fan rotating at 58.3 Hz was connected to the outlet of the hammer mill to control dust during operation, provide flowability of chopped biomass through the hammer mill, and collect the ground biomass (Fig. 2.2). A portion (25 kg) of each of the biomass ground in the hammer mill using 30 mm screen was sent to FPInnovations in Quebec City, Quebec for steam explosion pretreatment.

The power drawn by the chopper and hammer mill motors were measured using a wattmeter (Ohio Semitronics International, Hilliard, OH). The meter was connected to a data logging system (LABMATE Data Acquisition and Control System, Sciemetric Instruments, Ottawa,

ON), which transmitted time-power data to a desktop computer for recording and further analysis.

a) Six rotating chopper blades inclined at an angle of 14° with horizontal axis of rotation

b) Feed hopper and rollers to feed the material for chopping



c) Biomass chopper assembly

Figure 2.1: Biomass chopper fabricated at the Department of Agricultural and Bioresource Engineering, University of Saskatchewan, Canada.

Figure 2.2: Hammer mill and dust collector system employed to grind non-treated and steam exploded barley, canola, oat and wheat straw using various screen sizes.

2.3.2 Steam Explosion of Agricultural Biomass

The steam explosion of ground straw obtained using 30 mm hammer mill screen size was performed at the pilot-scale continuous steam explosion plant of FPInnovations, Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized disc refiner having a plate gap of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive set to operate at 33.3 Hz. The biomass flow through the refiner is wet (in suspension). The throughput of the equipment can vary between 50 and 200 kg of dried material per hour, depending on the bulk density of the raw material and the desired final particle size of the steam exploded material. The feed rate of agricultural straw into the digester was controlled using a plug screw feeder. The digester was operated at 180^{o}C (steam pressure of 900 kPa) for 4 min to perform steam explosion of the agricultural biomass. A flash tube convective dryer having 90 m long tube was used to dry the steam exploded barley, canola, oat and wheat straw at an average moisture

content of 70.1%, 80.7%, 76.7%, and 81.0% (wb) to approximately an average moisture content of 12.2, 13.6, 12.0 and 12.0% (wb), respectively. The direct heating of air was performed using 1172 kW natural gas burner, which has variable control to operate at different temperatures.

During the transportation of steam exploded material from Quebec City, Quebec to Saskatoon, Saskatchewan, the average moisture content of steam exploded barley, canola, oat and wheat straw was reduced to 7.8, 6.2, 6.8 and 7.0 % (wb), respectively. The steam exploded material was further ground in a hammer mill using three screen sizes of 6.4, 3.2 and 1.6 mm following the procedure described in the previous section.

2.3.3 Moisture Content

The moisture content of chopped straw, ground straw at hammer mill screen size of 30 mm and steam exploded biomass was determined using ASABE S358 (ASABE, 2006), where 25 g of material was oven-dried at 103^{o}C for 24 h. The moisture content of ground straw at hammer mill screen size of 6.4 mm was determined using AACC Standard 44-15A (AACC, 2005), where 3 g of material was oven-dried at 130^{o}C for 90 min. All of the moisture content tests were performed in replicates of three.

2.3.4 Chop and Particle Size Analysis

The geometric mean particle length of chopped agricultural straw samples and grinds from hammer mill screen size of 30 mm were determined using ASABE Standard S424 (ASABE, 2007). A set of 5 square-hole screens and a pan having widths of 406 mm and lengths of 565 mm were used for the tests. The screens had nominal opening sizes of 19.0, 12.7, 6.3, 3.96 and 1.17 mm. The screens were stacked over each other with the screen having largest opening size on top followed by other screens in decreasing opening size. Due to the low bulk density of the chopped material, only 750 g of material was placed at the top screen. The screen shaker was set to shake the screens for 5 min as suggested by the standard. The mass of the agricultural straw left over in each screen was determined and further calculations were performed to calculate the geometric mean particle length (X_{gm}) of the chopped agricultural straw. The tests were performed in replicates of three.

The geometric mean particle diameter of ground non-treated and steam exploded agricultural straw samples was determined using ASAE Standard S319 (ASABE, 2006). Due to low bulk density of steam exploded straw, only 50 g of ground sample was placed on a stack of sieves arranged from the largest to the smallest opening. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used particle size analysis. The sieve series selected were based on the range of particles in the samples. For grinds from 6.4 mm hammer mill screen opening, U.S. sieve numbers 10, 16, 20, 30, 50 and 70 (sieve opening sizes: 2.000, 1.190, 0.841, 0.595, 0.297 and 0.210 mm, respectively) were used. For grinds from 3.2 and 1.6 mm hammer mill screen openings, U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively) were used. A 10 min sieve shaking time was used as suggested in the ASAE Standard S319. The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated in replicates of three for each straw samples.

In this study, the authors have used the term "particle length" for chops obtained from the chopper and hammer mill having a screen size of 30 mm, and "particle diameter" for grinds obtained using hammer mill screen sizes of 6.4, 3.2 and 1.6 mm.

2.3.5 Bulk and Particle Density

Bulk density of hammer mill ground non-treated and steam exploded agricultural straw at three screen sizes of 6.4, 3.2 and 1.6 mm was determined by carefully filling a standard 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB) with sample. After filling every third portion of the container with ground straw sample, it was tapped on a wooden table for approximately 10 times to allow the material to settle down. After completely filling the container, excess material at the top was removed by moving a steel roller in a zig-zag pattern. The mass per unit volume gave the bulk density of the biomass in kg m^{-3}. A similar procedure was followed to determine the bulk density of hammer mill ground non-treated agricultural biomass at a screen size of 30 mm. In this case, a 2.9 L cylindrical container (fabricated in the Bioprocessing Lab, University of Saskatchewan) was used. A gas multi-pycnometer (QuantaChrome, Boynton Beach, FL) was used to determine the particle density of the hammer mill ground straw by calculating the displaced volume of nitrogen gas by a known

mass of material (Adapa et al., 2005). Three replicates for each sample were performed for both bulk and particle density measurements.

2.3.6 Specific Energy

During the chopping and grinding experiments, 3 kg each of either non-treated or steam exploded straw was manually fed into the chopper (Fig. 2.1) (no screen) and hammer mill (Fig. 2.2) having four screen sizes of 30, 6.4, 3.2 and 1.6 mm. The power drawn by the chopper and hammer mill motors, and the time required for the grinding process were measured and recorded. The power required to run empty chopper and hammer mill were recorded prior to the introduction of material in order to obtain base line data. This allowed determining the net power required to grind the material. The specific energy (kWh t^{-1}) required for chopping and grinding was determined by integrating the area under the power demand curve for the total time required to grind the sample for pre-determined quantity of material (Mani et al., 2004). Each test was performed in replicates of three.

Total specific energy required to grind non-treated straw can be obtained by adding specific energy required for chopping of the baled straw plus the specific energy required for hammer mill grinding.

Total specific energy required to grind steam exploded straw to 6.4, 3.2 and 1.6 mm hammer mill screen size can be obtained by adding specific energy required for chopping of the baled straw, specific energy for hammer mill grinding of straw at a screen size of 30 mm, and respective specific energy required for hammer mill grinding of steam exploded material at 6.4, 3.2 and 1.6 mm.

2.3.7 Statistical Analysis

The experiments were set up as completely random experimental design with 3 replications of specific energy and three-variable (straw, pre-treatment and hammer mill screen sizes) factorial design. Specific energy was the dependent variable, while pre-treatment and hammer mill screen sizes were the independent variables. Statistical analyses were conducted using SAS for Windows (version 8.2) (SAS, 1999). In order to further understand and explain the experimental variables and their interactions, the SAS general linear model (GLM) for completely randomized

design (CRD) procedure was used and the Student-Neuman-Keuls test (SNK) was performed on non-treated and steam exploded agricultural biomass. SNK determines the difference between any two treatment means at 5% level of significance (SAS, 1999). Best predictor equations for bulk and particle density of hammer mill ground non-treated and steam exploded material, and specific energy required for grinding were developed with the highest coefficient of determination (R^2) with geometric mean particle size (result of various hammer mill screen sizes) being the independent variable. The equation parameters were estimated using MS Excel software and SAS software for Windows (version 8.2) (Statistical Analysis System, Cary, NC) (SAS, 1999).

In addition, test of normality for particle size distribution (percentage mass of grinds retained over the sieves using ASAE Standard S319 (ASABE, 2006)] of non-treated and steam exploded grinds obtained from hammer mill screen sizes of 6.4, 3.2 and 1.6 mm were performed using Proc Univariate Normal Plot analysis in SAS (SAS, 1999). The analysis of the mass retained on the sieves was performed using three methods, namely: Shapiro-Wilk test, and determination of skewness and kurtosis values. The Shapiro-Wilk statistic (W) can be used to test if the observations follow a normal distribution and the probability (P value) is used to accept or reject the hypothesis of whether the data is normally distributed or not. The data is normally distributed if $P > 0.05$. Skewness and Kurtosis are two measures of departure from a normal distribution; both statistics will be equal to zero if the data is normally distributed.

Figure 2.3 shows the photograph of non-treated (at hammer mill screen size of 30 mm) and steam exploded barley, canola, oat and wheat straw grinds.

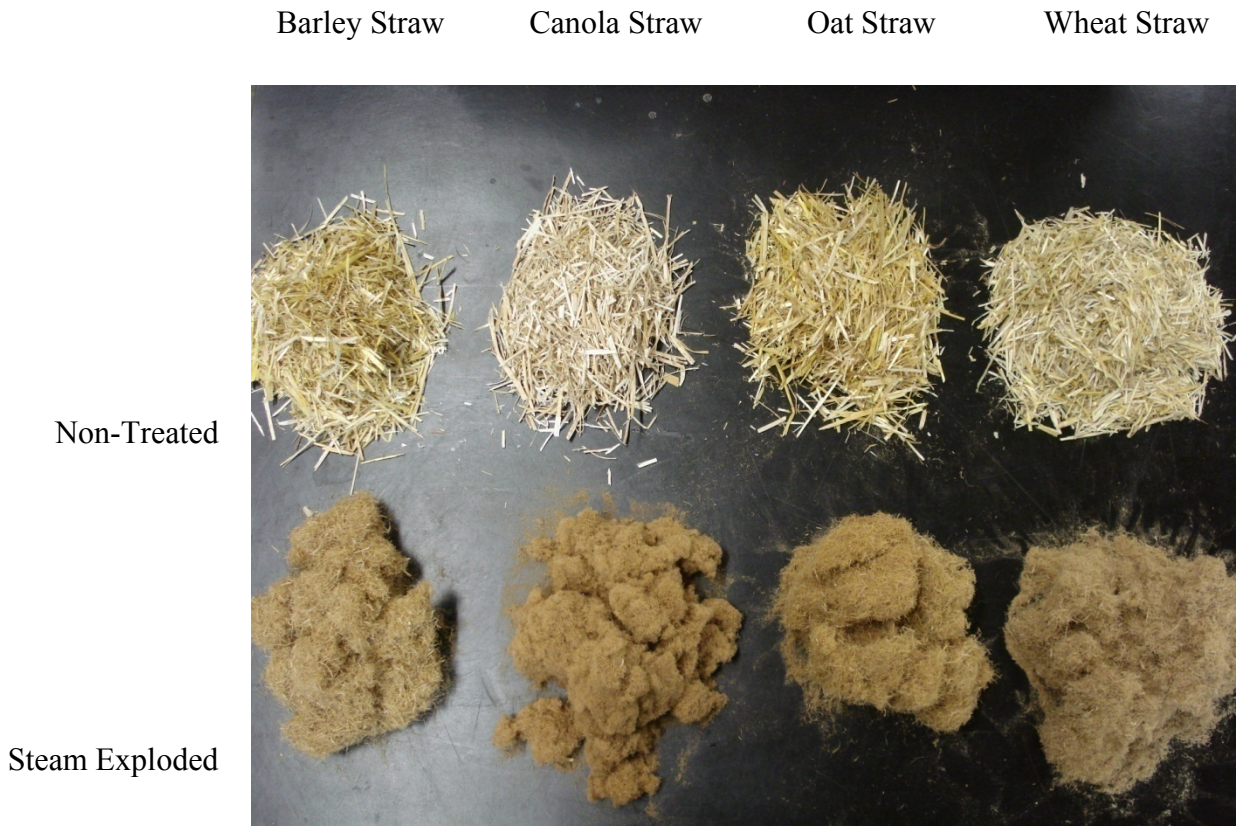


Figure 2.3: Photographs showing the non-treated (30 mm hammer mill screen size) and steam exploded barley, canola, oat and wheat straw grinds.

2.4 Results and Discussion

2.4.1 Geometric Mean Particle Size

The geometric mean chop length or particle diameter of non-treated and steam exploded barley, canola, oat and wheat straws are shown in Table 2.1. The mean geometric particle size for any particular biomass decreased with a decrease in hammer mill screen size from 6.4 to 1.6 mm. The decrease in mean particle diameter was significant for non-treated canola and wheat straw, and steam exploded barley, oat and wheat straw; however, non-treated barley and oat straw, and

steam exploded canola straw at hammer mill screen sizes of 3.2 and 1.6 mm did not show a significant change.

The geometric mean particle size of steam exploded straw at any specific hammer mill screen size was significantly smaller than that of the non-treated straw. This could be due to the fact that application of steam explosion pre-treatment disintegrates the lignocellulosic structure of the biomass (Sokhansanj et al., 2005) leading to lower shear strength (easier to grind the straw).

Table 2.2 and Figure 2.4 represents the measure of particle size distribution of selected biomass grinds obtained from hammer mill using three different screen sizes of 6.4, 3.2 and 1.6 mm. Using the Shapiro-Wilk test, it has been determined that the non-treated barley and wheat straw grinds obtained from 6.4 mm screen hammer mill are not normally distributed ($P < 0.05$), skewed towards right (positive values) and higher peaks than expected for the normal distribution (positive value). It has been reported that wider particle size distribution is suitable for compaction (pelleting/briquetting) process (Mani et al., 2004). During compaction, smaller (fine) particles rearrange and fill in the void space of larger (coarse) particles producing denser and durable compacts (Tabil, 1996). Therefore, ideally the grinds should be normally distributed (Shapiro-Wilk test: $P > 0.05$), should have near zero skewness and lower peak than expected for the normal and wider distribution of data (negative Kurtosis values). Upon application of this concept on Table 2, it can be deduced that for non-treated barley straw at 1.6 mm hammer mill screen size ($P > 0.05$; Skewness = 0.276; Kurtosis = -1.875), canola straw ($P > 0.05$; Skewness = 0.039; Kurtosis = -2.774), oat straw ($P > 0.05$; Skewness = -0.080; Kurtosis = -2.912), and wheat straw ($P > 0.05$; Skewness = 0.554; Kurtosis = -1.862) at 3.2 mm hammer mill screen size resulted in grinds that would potentially produce better compacts. For steam exploded agricultural biomass, Table 2.2 also shows that barley ($P > 0.05$; Skewness = -0.097; Kurtosis = -1.077), canola ($P > 0.05$; Skewness = -0.202; Kurtosis = -2.725) and wheat ($P > 0.05$; Skewness = 0.652; Kurtosis = 0.044) straw at 6.4 mm hammer mill screen size, and oat ($P > 0.05$; Skewness = 0.088; Kurtosis = -1.272) straw at 1.6 mm screen size would potentially produce better compacts.

Table 2.1: Specific energy, geometric mean particle size, and bulk and particles densities of selected non-treated and steam exploded agricultural biomass.

Biomass	Hammer Mill Screen Size (mm)	Moisture Content (%, wb) ‡†	Geometric Mean Particle Diameter or Chop Length (mm) ‡†	Bulk Density (kg m^{-3}) ‡†	Particle Density (kg m^{-3}) ‡†	Average Feed Rate (kg h^{-1})	Specific Energy - Chopping/ Grinding (kWh t^{-1}) ‡ †
Non-Treated Agricultural Biomass							
Barley	Chops	13.5±0.1 ɵ †	3.373±0.292* D£	ND	ND	78	3.15±0.09 aD
	30	13.5±0.1 ɵ	1.815±0.146* aD	65±01 aD	809±19 aD	224	1.70±0.29 aD
	6.4	12.4±0.0 ɵ ɵ	0.883±0.025¥ bD	96±02 bDX	1016±137 bDEX	74	8.26±1.94 bDX
	3.2	ND	0.463±0.016¥ cD	149±03 cDEX	1089±32 bDX	63	18.59±1.77 cDX
	1.6	ND	0.456±0.004¥ cD	155±01 dDX	1149±02 bDX	25	25.10±0.82 dDX
Canola	Chops	15.1±0.1	2.415±0.019 E	ND	ND	85	1.96±0.33 aE
	30	15.1±0.1	1.285±0.007 aE	80±04 aE	907±06 aE	138	1.46±0.30 aD
	6.4	13.4±0.1	0.885±0.020 bD	144±02 bEX	1019±19 bDEX	67	12.38±1.42 bEX
	3.2	ND	0.521±0.061 cDE	190±09 cFX	1192±11 cEX	46	25.73±1.00 cEX
	1.6	ND	0.367±0.001 dE	203±11 cEX	1309±02 dEX	38	35.70±8.64 dEX
Oat	Chops	13.1±0.1	4.153±0.379 F	ND	ND	115	2.74±0.37 aDF
	30	13.1±0.1	2.237±0.122 aF	69±02 aD	787±17 aD	202	5.68±0.83 aE
	6.4	10.3±0.2	0.935±0.013 bD	111±08 bFX	873±18 bEX	88	16.23±1.68 bFX
	3.2	ND	0.566±0.015 cE	156±04 cDX	1093±38 cDX	53	29.62±2.92 cEX
	1.6	ND	0.404±0.014 cF	196±04 dEX	1240±18 dFX	24	41.52±6.10 dEX
Wheat	Chops	15.6±0.2	4.220±0.295 F	ND	ND	119	2.27±0.06 aEF
	30	15.6±0.2	1.843±0.015 aD	59±01 aF	880±58 aE	200	2.05±0.70 aD
	6.4	13.3±0.1	0.997±0.038 bE	107±02 bFX	1078±14 bDX	90	12.26±0.70 bEX
	3.2	ND	0.719±0.015 cF	141±02 cEX	1225±11 cEX	44	28.02±2.87 cEX
	1.6	ND	0.452±0.016 dD	154±02 dDX	1269±23 cDX	25	42.57±2.04 dEX
Steam Exploded Agricultural Biomass							
Barley	UG	7.8±0.1 ɵ	ND	ND	ND	NA	NA
	6.4	5.8±0.3 ɵ ɵ	0.607±0.028 aD£¥	38±03 aDY	1033±19 aDX	49	8.05±1.31 aDX
	3.2	ND	0.368±0.002 bD¥	73±02 bDY	1342±60 bDY	43	20.43±4.18 bDX
	1.6	ND	0.296±0.013 cD¥	93±06 cDY	1415±79 bDY	32	30.13±4.99 cDX

Canola	UG	6.2±0.1	ND	ND	ND	NA	NA
	6.4	4.3±0.0	0.698±0.127 aD	33±02 aEY	968±38 aDX	64	2.69±0.26 aEY
	3.2	ND	0.447±0.010 bE	44±00 bEY	1138±17 bEY	50	5.79±0.34 aEY
	1.6 (UC)	ND	0.364±0.007 bE	67±02 cEY	1294±17 cDX	35	27.90±6.37 bDX
Oat	UG	6.8±0.7	ND	ND	ND	NA	NA
	6.4	4.6±0.1	0.602±0.012 aD	43±01 aFY	1143±23 aEY	60	10.06±0.15 aFY
	3.2	ND	0.367±0.010 bD	77±04 bDY	1272±13 bDY	46	19.50±2.13 bDY
	1.6	ND	0.327±0.022 cD	91±03 cDY	1368±18 cDY	31	33.18±3.10 cDX
Wheat	UG	7.0±1.3	ND	ND	ND	NA	NA
	6.4	4.5±0.2	0.568±0.10 aD	41±01 aDFY	1119±52 aEX	52	7.34±1.20 aDY
	3.2	ND	0.387±0.005 bF	73±05 bDY	1314±32 bDY	45	14.73±1.25 bFY
	1.6	ND	0.309±0.012 cD	100±05 cDY	1380±80 bDX	35	25.99±0.85 cDY

UG – Un-ground Steam exploded material; UC – Un-controlled steam explosion test (retention time inside the digester was about 10 min); ND – Not determined either due to large geometric mean chop length or fibrous nature of the steam exploded material; NA – Not applicable

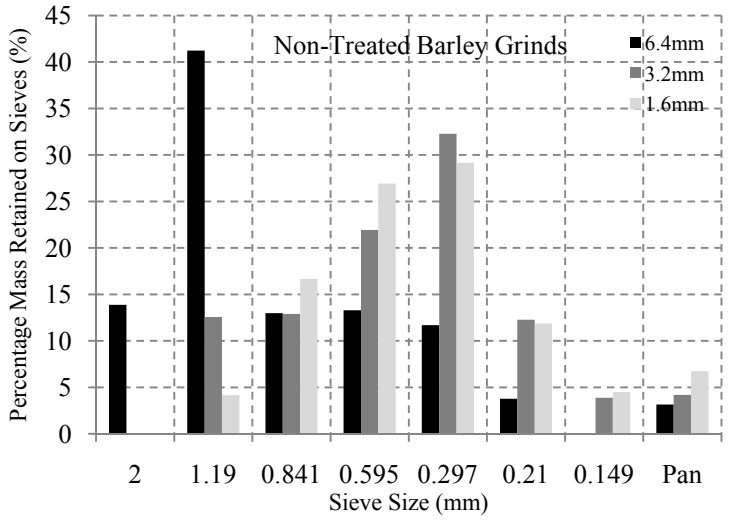
‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass at various hammer mill screen sizes (a, b and c); at same hammer mill screen sizes for different sample biomass (D, E and F); for any particular biomass at same hammer mill screen size for non-treated and steam exploded biomass (X and Y)

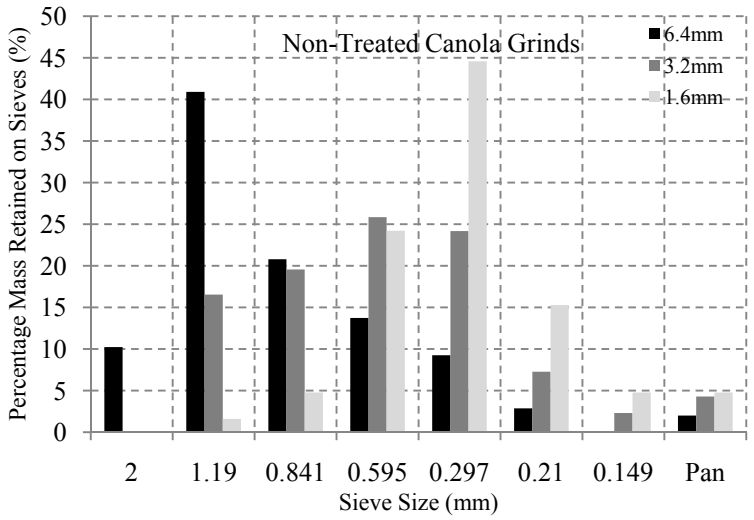
ɵ ASAE Standards 358.2 (2006); ɵ ɵ AACC Standard 44-15A (2005); * ASABE Standard S424.1 (2007); ¥ASABE Standard S319.3 (2001)

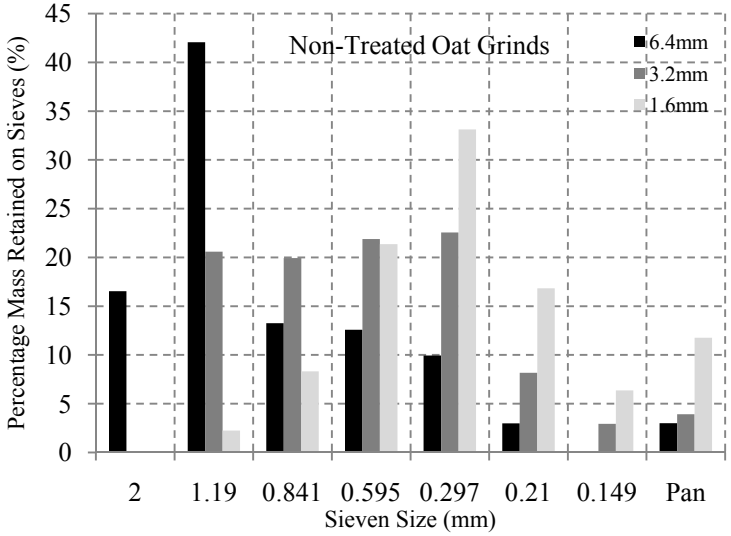
Table 2.2: Measure of particle size distribution of selected non-treated and steam exploded agricultural biomass grinds obtained from hammer mill using three different screen sizes.

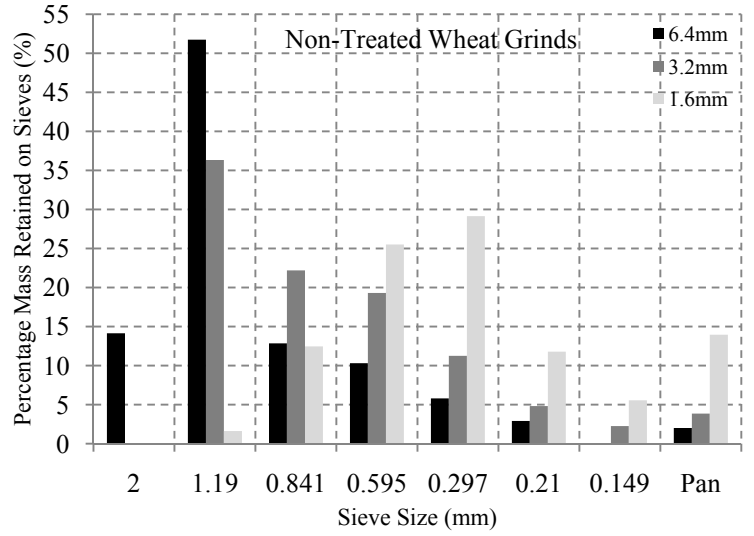
Biomass	Hammer mill screen size (mm)	Shapiro-Wilk Test‡	Skewness†	Kurtosis*	Observation
Non-Treated Agricultural Biomass					
Barley	6.4	W = 0.735; P = 0.014	1.956	4.577	P < 0.05
	3.2	W = 0.906; P = 0.408	0.804	-0.182	P > 0.05
	1.6	W = 0.921; P = 0.509	0.276	-1.875	P > 0.05
Canola	6.4	W = 0.874; P = 0.241	1.482	2.398	P > 0.05
	3.2	W = 0.859; P = 0.189	0.039	-2.774	P > 0.05
	1.6	W = 0.804; P = 0.065	1.413	1.543	P > 0.05
Oat	6.4	W = 0.813; P = 0.077	1.767	3.864	P > 0.05
	3.2	W = 0.827; P = 0.101	-0.080	-2.912	P > 0.05
	1.6	W = 0.929; P = 0.579	0.979	0.631	P > 0.05
Wheat	6.4	W = 0.717; P = 0.009	2.153	4.931	P < 0.05
	3.2	W = 0.886; P = 0.299	0.554	-1.862	P > 0.05
	1.6	W = 0.885; P = 0.292	0.602	-1.352	P > 0.05
Steam Exploded Agricultural Biomass					
Barley	6.4	W = 0.964; P = 0.848	-0.097	-1.077	P > 0.05
	3.2	W = 0.880; P = 0.270	1.287	1.927	P > 0.05
	1.6	W = 0.943; P = 0.687	0.809	-0.034	P > 0.05
Canola	6.4	W = 0.831; P = 0.110	-0.202	-2.725	P > 0.05
	3.2	W = 0.974; P = 0.920	-0.148	-1.153	P > 0.05
	1.6	W = 0.979; P = 0.948	0.446	-0.197	P > 0.05
Oat	6.4	W = 0.984; P = 0.972	0.220	-0.170	P > 0.05
	3.2	W = 0.878; P = 0.261	1.366	2.778	P > 0.05
	1.6	W = 0.961; P = 0.824	0.088	-1.272	P > 0.05
Wheat	6.4	W = 0.926; P = 0.547	0.652	0.044	P > 0.05
	3.2	W = 0.921; P = 0.514	0.966	1.667	P > 0.05
	1.6	W = 0.948; P = 0.721	0.952	1.053	P > 0.05

‡Shapiro-Wilk Test: Data is normally distributed if P > 0.05; W is statistical value of the test; P is the probability value used to accept or reject the hypothesis of whether the data is normally distributed or not
†Skewness: Skewness to the left (negative value); Skewness to the right (positive value)
*Kurtosis: Peak is lower than expected for the normal (negative value); peak is higher than expected for the normal distribution (positive value)

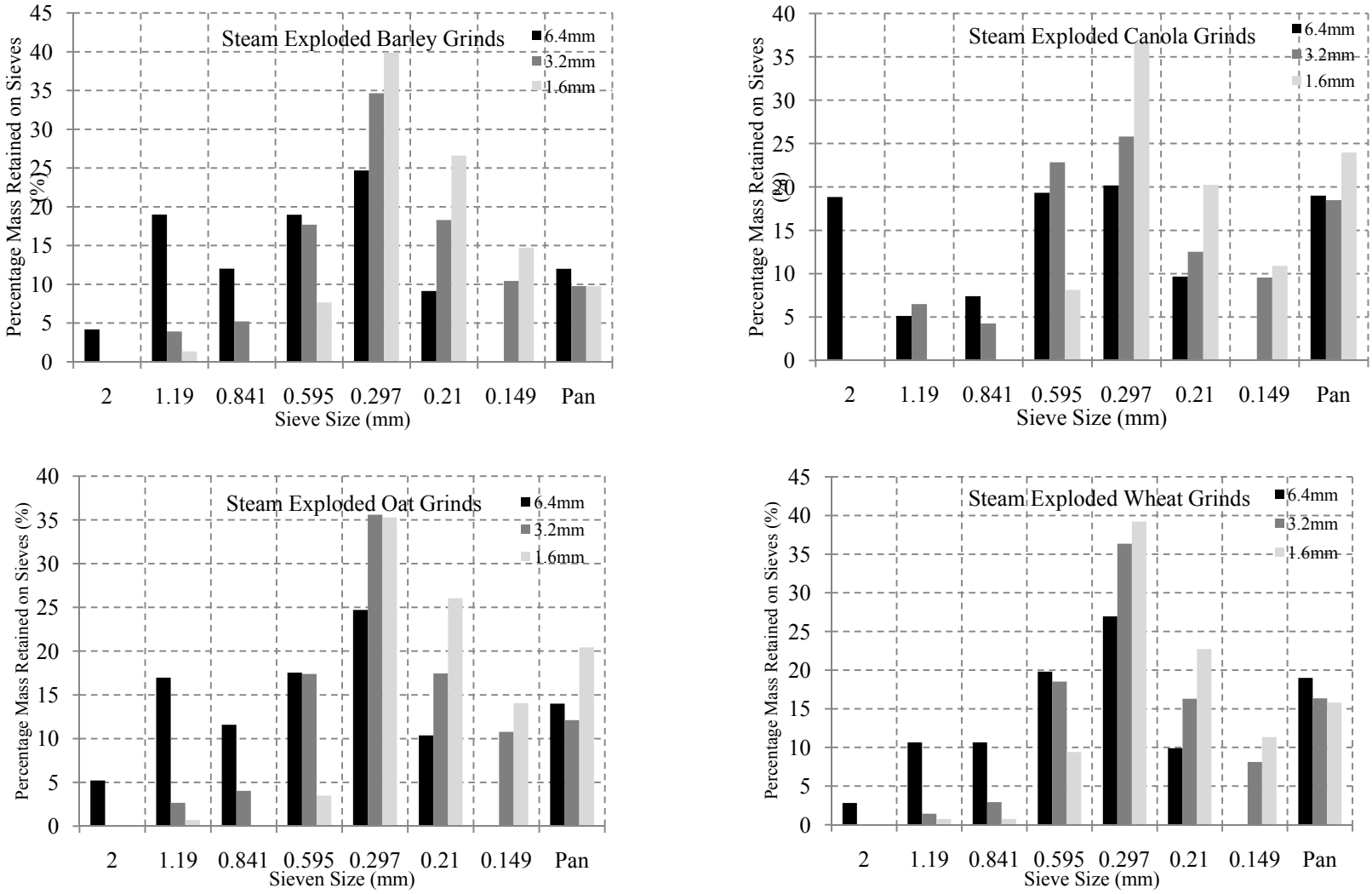








(a) Non-Treated Agricultural Biomass



(b) Steam Exploded Agricultural Biomass

Figure 2.4: Percentage mass retained over sieves representing the particle size distribution of selected non-treated and steam exploded agricultural biomass ground using three different hammer mill screen sizes of 6.4, 3.2 and 1.6 mm.

2.4.2 Bulk Density

The bulk density values for barley, canola, oat and wheat straw chops and grinds are given in Table 2.1. The bulk density of non-treated and steam exploded straw significantly increased with a decrease in hammer mill screen size from 6.4 to 1.6 mm, except for non-treated canola straw at 3.2 and 1.6 mm.

The bulk density of non-treated barley, canola, oat and wheat straw at any specific hammer mill screen size was significantly higher than steam exploded straw (Table 2.1). This could again be attributed to the fact that application of steam explosion pre-treatment disintegrates the organized and compact lignocellulosic structure of biomass leading to lower bulk densities. The average bulk density of non-treated barley, canola, oat and wheat straw for 6.4, 3.2 and 1.6 mm hammer mill screen sizes was 153, 104 and 66%, 340, 331, 205%, 157, 104 and 116%, and 162, 94 and 53%, higher than steam exploded straw, respectively.

Figure 2.5 shows the change in bulk density of non-treated and steam exploded biomass grinds as a function of geometric mean particle diameter. The best predictor equations having highest R^2 values of 0.99, 0.95, 0.99 and 0.99 were obtained for non-treated barley, canola, oat and wheat straw, respectively, while highest R^2 values of 0.98, 0.90, 0.99 and 0.99 were obtained for steam exploded barley, canola, oat and wheat straw, respectively.

2.4.3 Particle Density

The particle density of non-treated and steam exploded barley, canola, oat and wheat straw significantly increased with a decrease in hammer mill screen size from 30 to 1.6 mm (Table 2.1), with some exception.

The particle density of steam exploded barley and oat straw was significantly higher than non-treated straw (Table 2.1). Again, this could be the result of steam explosion process where the organized lignocellulosic structure is disintegrated into finer components (Figure 2.3). The particle density of steam exploded canola straw was lower and wheat straw was higher, however, not statistically different with non-treated straw. The average particle density of steam exploded

barley, oat and wheat straw for 6.4, 3.2 and 1.6 mm hammer mill screen sizes was 2, 23 and 23%, 31, 16 and 10%, and 4, 7 and 9%, higher than non-treated straw, respectively. However, the average particle density of steam exploded canola straw for 6.4, 3.2 and 1.6 mm was 5, 5 and 1%, lower than non-treated canola straw, respectively (Table 2.1).

Figure 2.6 shows the variation in particle density as a function geometric mean particle diameter of non-treated and steam exploded biomass grinds. The best predictor equations having highest R^2 values of 0.82, 0.99, 0.91 and 0.94 were obtained for non-treated barley, canola, oat and wheat straw, respectively, while highest R^2 values of 0.93, 0.95, 0.92 and 0.85 were obtained for steam exploded barley, canola, oat and wheat straw, respectively.

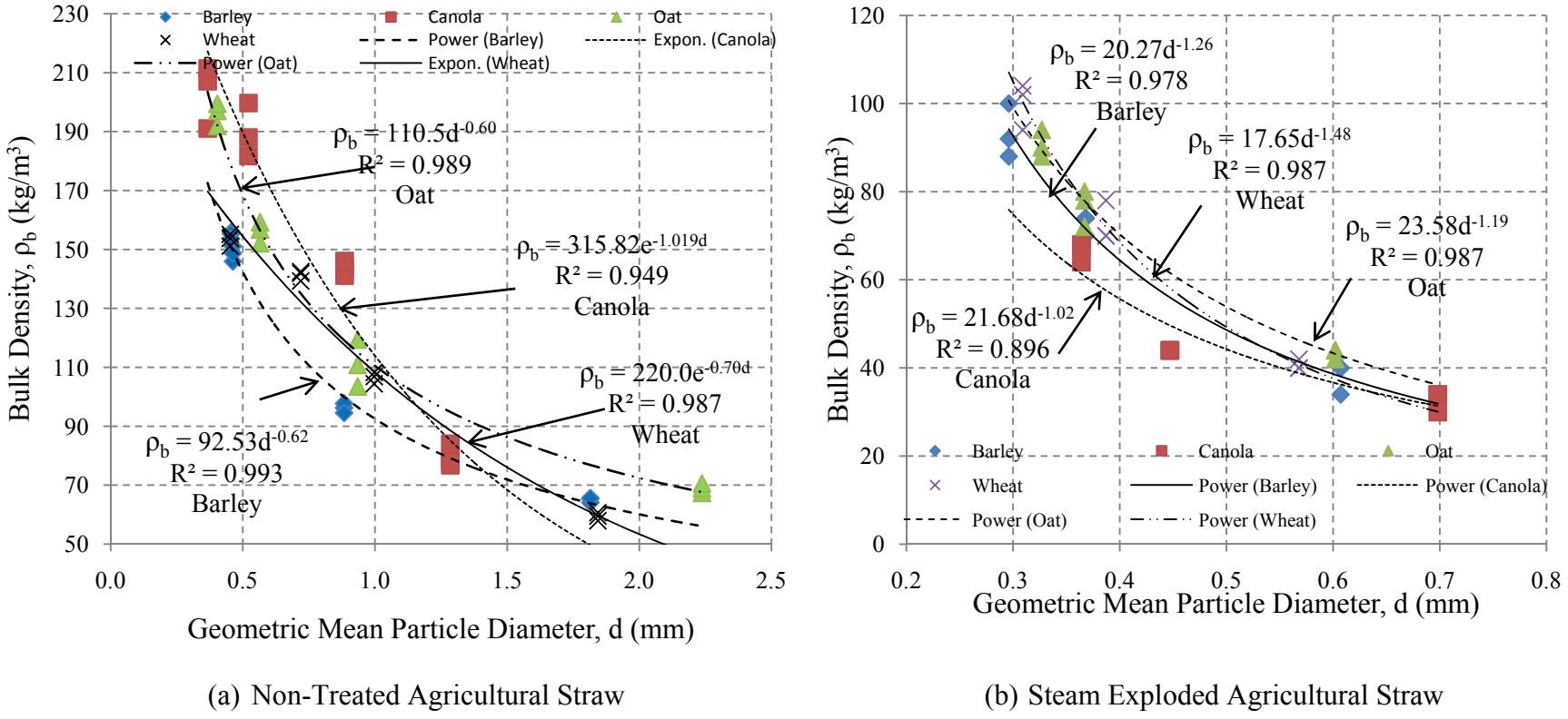
2.4.4 Specific Energy

Table 2.1 also shows the specific energy requirements of the chopper and hammer mill to grind barley, canola, oat and wheat straw at average moisture contents of 13.5, 15.1, 13.1 and 15.6% (wb), respectively. The chopper consumed the highest (3.15±0.09 kWh t^{-1}) and the lowest (1.96±0.33 kWh t^{-1}) specific energy to chop barley and canola straw, respectively. The specific energy required to grind agricultural biomass significantly increased with a decrease in hammer mill screen size from 30 to 1.6 mm due to the fact that the material throughput decreases with a decrease in screen size.

The specific energy required by hammer mill to grind non-treated and steam exploded barley, canola, oat and wheat straws showed a negative power correlation with hammer mill screen sizes (Figure 2.7). It has also been observed that the specific energy required to grind non-treated and steam exploded agricultural biomass from 6.4 to 1.6 mm hammer mill screen size increased by 204, 188, 156 and 247%, and 274, 937, 230 and 254% for barley, canola, oat and wheat straw, respectively. An unusually high increase of 937% could be a result of un-controlled steam explosion of a portion of canola straw, which was retained in the digester for approximately 10 min (5 min higher than specified limit for the tests) due to clogging of the material. The results reported in this study are similar to the power equation obtained for oat straw (Soucek et al., 2003). However, two other studies reported a second-order polynomial relationship between the specific energy requirements (Mani et al., 2004; Sitkei, 1986).

The specific energy required to grind non-treated and steam exploded barley straw using 6.4, 3.2 and 1.6 mm hammer mill screen sizes was not statistically different (Table 2.1). However, the steam exploded barley straw at 6.4 mm hammer mill screen size consumed on an average 3% lower specific energy, while at 3.2 and 1.6 mm screen size consumed 9 and 17% higher specific energy as compared to non-treated barley straw. The average specific energy required to grind steam exploded canola, oat and wheat straw for 6.4, 3.2 and 1.6 mm hammer mill screen sizes was 360, 344 and 28%, 61, 52 and 25%, and 67, 90 and 64% lower than non-treated straw, respectively (Table 2.1). During steam explosion process the organized lignocellulosic matrix disintegrates into finer components hence requiring lower specific energy for grinding purpose. It has been observed that the steam explosion treatment has relatively significant impact on grinding of canola straw.

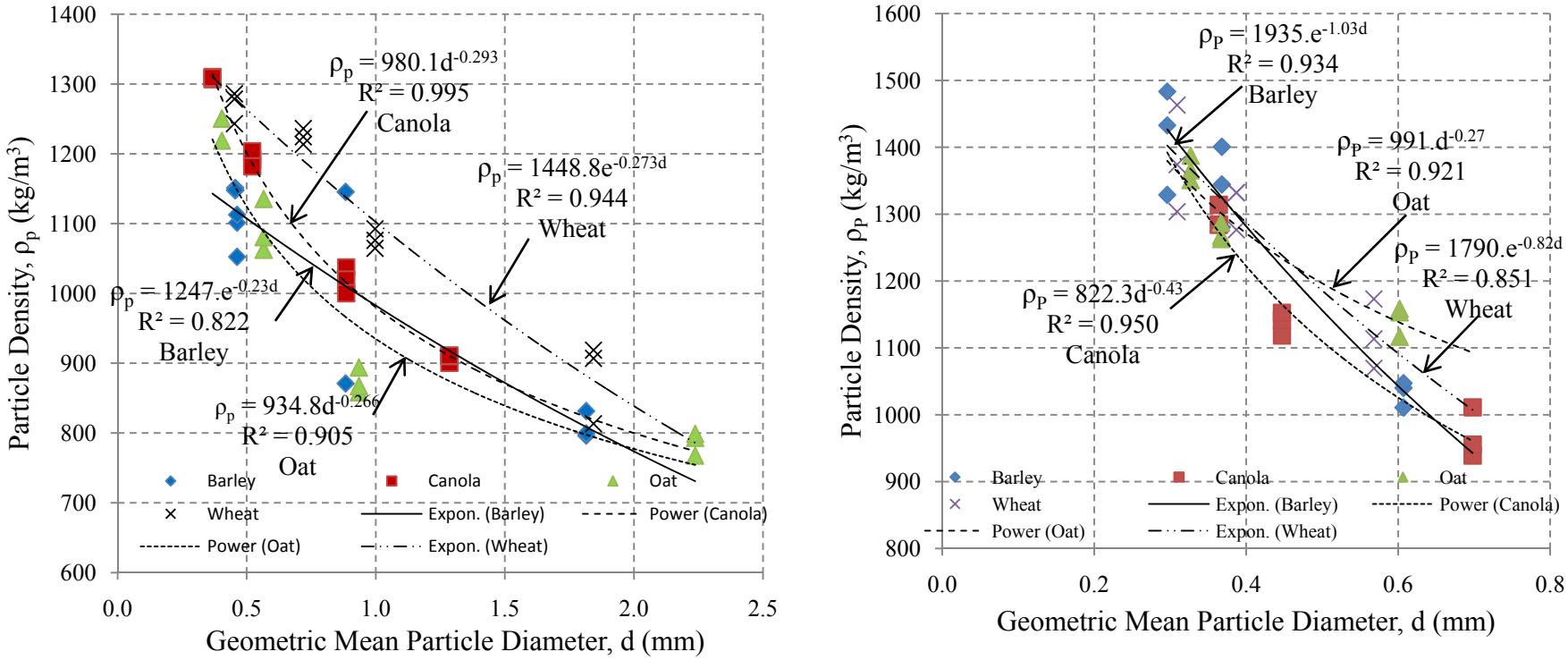
The specific energy required to reduce the particle size of non-treated and steam exploded biomass as affected by hammer mill screen sizes is shown in Figure 2.7. The best predictor equations having highest R^2 values of 0.97, 0.96, 0.98 and 0.97 were obtained for non-treated barley, canola, oat and wheat straw, respectively, while highest R^2 values of 0.93, 0.95, 0.98 and 0.97 were obtained for steam exploded barley, canola, oat and wheat straw, respectively.



(a) Non-Treated Agricultural Straw

(b) Steam Exploded Agricultural Straw

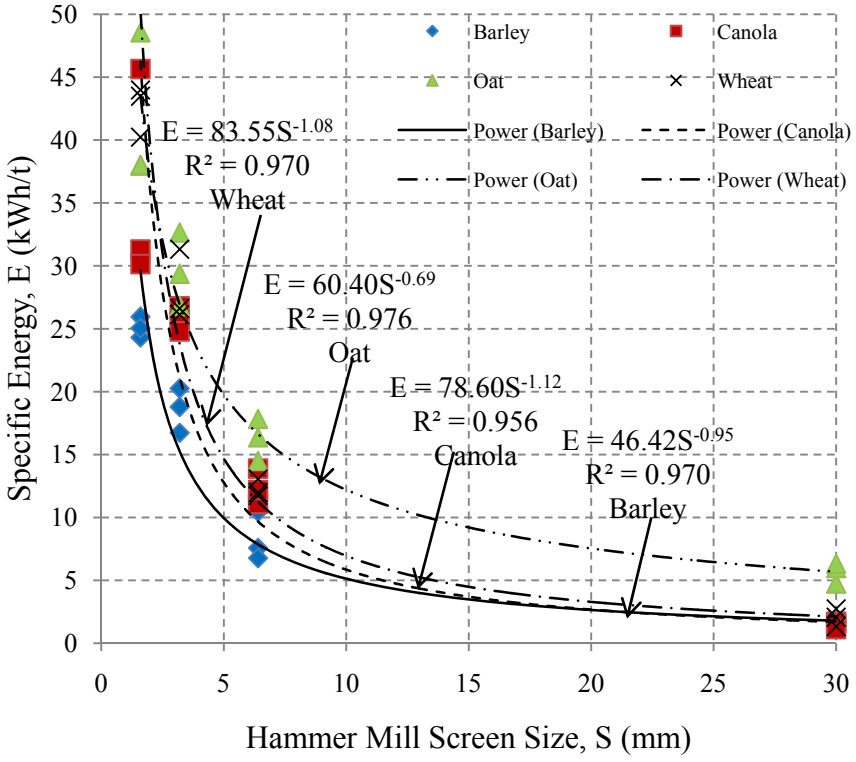
Figure 2.5: Bulk density (ρ_b) as a function of geometric mean particle diameter (d) for non-treated and selected steam exploded agricultural biomass grinds obtained from three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm.



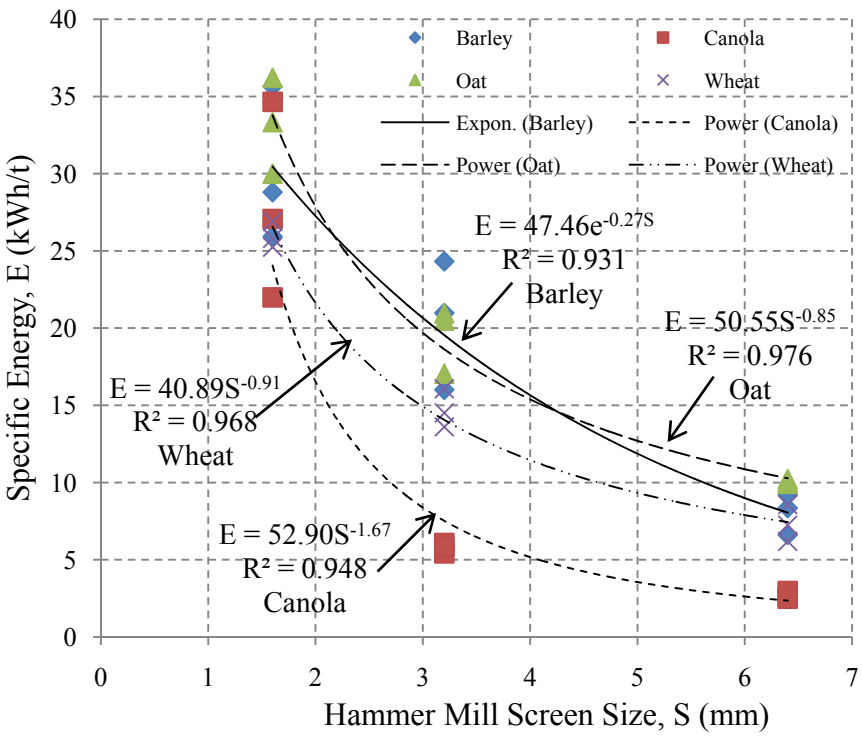
(a) Non-Treated Agricultural Straw

(b) Steam Exploded Agricultural Straw

Figure 2.6: Particle density (ρ_p) as a function of geometric mean particle diameter (d) for selected non-treated and steam exploded agricultural biomass grinds obtained from three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm.



(a) Non-Treated Agricultural Straw



(b) Steam Exploded Agricultural Straw

Figure 2.7: Specific energy (E) required for grinding selected non-treated and steam exploded agricultural biomass using three hammer mill screen sizes (S) of 6.4, 3.2 and 1.6 mm.

2.5 Conclusion

In the present study, the grinding performance of a chopper and hammer mill, and physical characteristics of non-treated and steam exploded barley, canola, oat and wheat straw were successfully determined. The following conclusions were drawn:

1. The bulk density of non-treated biomass was significantly higher than the bulk density of steam exploded agricultural biomass for similar hammer mill screen sizes.

2. The particle density of steam exploded barley and oat straw was significantly higher than non-treated straw, except at barley 6.4 mm hammer mill screen size. The particle density of steam exploded canola straw was lower and wheat straw was higher, however, not statistically different with non-treated straw, except at canola and wheat at 3.2 mm hammer mill screen size.

3. The specific energy values required to hammer mill non-treated and steam exploded barley straw were not statistically different. The specific energy required for grinding steam exploded canola, oat and wheat straw was significantly lower than non-treated straw, except for canola and oat straw at 1.6 mm hammer mill screen size. However, it should be noted that it is possible to control the final grind size of the steam exploded material by controlling the material feed rate using the plug screw feeder into the digester, which could potentially allow one to entirely eliminate the need to grind the steam exploded agricultural material in future.

Chapter 3

3. Physical and Frictional Properties of Ground Non-Treated and Steam Exploded Barley, Canola, Oat and Wheat Straw Grinds

A similar version of this chapter has been published in Powder Technology:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2010. Physical and frictional properties of ground non-treated and steam exploded barley, canola, oat and wheat straw grinds. *Powder Technology*, 201: 230-241.

Contributions of Ph.D. Candidate

The present study resulted in development of baseline data and correlations that could be used to predict coefficient of internal friction, and cohesion coefficient with respect to the geometric mean particle size of non-treated and steam exploded barley, canola, oat and wheat straw grinds. The frictional properties of agricultural biomass can be used by manufacturers to design new and modify existing bins, hoppers and feeders for handling and storage of straw for biofuel industry. All of the experiments, data analysis and manuscript writing were performed by Phani Adapa with the assistance of Dallas Nelson (Summer Research Assistant), while Dr. Lope Tabil and Dr. Greg Schoenau provided editorial input.

Contribution of this Paper to Overall Study

Knowledge Gap: In literature, the coefficient of internal friction has been reported for peanut hull, switchgrass, poultry litter, chopped switchgrass, wheat straw and corn stover. However, no studies were found on internal friction and cohesion properties of non-treated and steam exploded barley, canola, oat and wheat straw grinds. Therefore, the objective of present study was to determine the effect of steam explosion pretreatment, hammer mill screen size, and normal forces on the coefficient of internal friction and cohesion properties of non-treated and steam exploded barley, canola, oat and wheat straw grinds.

Justification: Prior to densification, biomass grinds need to be efficiently stored, handled and transported. Physical and frictional properties of biomass have significant effect on design of new and modification of existing bins, hoppers and feeders (Fasina et al., 2006). The frictional behavior of biomass grinds in all engineering applications is described by two independent parameters: the coefficient of internal friction, and the coefficient of wall friction. The former determines the stress distribution within particles undergoing strain, and the latter describes the magnitude of the stresses between the particle and the walls of its container (Seville et al., 1997).

3.1 Abstract

During storage and handling, accurate knowledge of the physical and frictional behavior of biomass grinds is essential for the efficient design of equipment. Therefore, experiments were performed on non-treated and steam exploded barley, canola, oat and wheat straw grinds to determine their coefficient of internal friction and cohesion at three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm, three normal stress values of 9.8, 19.6 and 39.2 kPa at 10% moisture content (wb). At any specific hammer mill screen size, the geometric mean particle size and bulk density of non-treated straw was significantly larger than steam exploded straw. The bulk density of ground straw significantly increased with a decrease in hammer mill screen sizes. The steam exploded straw grinds resulted in higher coefficient of internal friction compared to non-treated straw grinds primarily because of lower bulk densities. The coefficient of friction for non-treated barley, canola, oat and wheat straw were in the range of 0.505 to 0.584, 0.661 to

0.665, 0.498 to 0.590, and 0.532 to 0.591, respectively. Similarly, the coefficient of friction for steam exploded barley, canola, oat and wheat straw were in the range of 0.562 to 0.738, 0.708 to 0.841, 0.660 to 0.860, and 0.616 to 1.036, respectively, which were higher than non-treated straw of the kind. Power, logarithmic or exponential equations were developed to predict the coefficient of internal friction and cohesion with respect to average geometric mean particle diameters for non-treated and steam explode barley, canola, oat and wheat straw grinds.

3.2 Introduction

Efficient and economic production and processing of agricultural biomass residue as feedstock is critical for the viability of a biofuel industry (Campbell et al., 2002; Sokhansanj et al., 2006). Due to their heterogeneous nature, agricultural biomass materials possess inherently low bulk densities, and often require densification to improve their handling characteristics and logistics of transportation and storage (Mani et al., 2004; Shaw and Tabil, 2006). The bulk density of loose and standard baled straw is approximately 40 kg/m^3 and 100 kg/m^3, respectively, compared with the bulk density of unprocessed wood residue, which is approximately 250 kg/m^3 (Demirbas, 2001; Tripathi et al., 1998). Fuels with high bulk density are advantageous because they represent a high energy-for-volume value. Consequently, these fuels need less storage space for a given refueling time. Inadequate bulk densities can be improved by either briquetting or pelleting of the biomass (FAO, 2007; Rajvanshi, 1986). A bulk density of 650 kg/m^3 is stated as design value for wood pellet producers (Obernberger and Thek, 2004).

Prior to densification, biomass grinds need to be efficiently stored, handled and transported. Physical and frictional properties of biomass have significant effect on design of new and modification of existing bins, hoppers and feeders (Fasina et al., 2006). The frictional behavior of biomass grinds in all engineering applications is described by two independent parameters: the coefficient of internal friction, and the coefficient of wall friction. The former determines the stress distribution within particles undergoing strain, and the latter describes the magnitude of the stresses between the particle and the walls of its container (Seville et al., 1997). The classic law of friction states that frictional force is directly proportional to the total force that acts normal to the shear surfaces (Larsson, 2010). Frictional force depends on the nature of the materials in

contact but is independent of the area of contact or sliding velocity (Mohsenin, 1886). Material properties such as moisture content and particle size affect the frictional properties and densification performance of an individual feedstock (Larsson, 2010; Shaw and Tabil, 2006). In addition, the determination of coefficient of friction is essential for the design of production and handling equipment and in storage structures (Puchalski and Brusewitz, 1996).

Mani et al. (2004) studied the coefficient of wall friction properties of corn stover at two grind sizes of 6.35 and 3.18 mm, and three moisture contents of 7, 11 and 15% (wb) on a galvanized steel surface. It was observed that the adhesion coefficient did not exhibit dependence on moisture content. The coefficient of wall friction of corn stover grind increased from 0.18 to 0.26 with an increase in moisture content from 7% to 15%. No clear trend was observed for the adhesion coefficient.

Shaw and Tabil (2006) performed studies to determine the mechanical properties of peat moss, wheat straw, oat hulls and flax shives at 9-10% moisture content (wb) having geometric mean particle sizes of 0.74, 0.65, 0.47 and 0.64 mm, respectively, on a mild steel surface. It was found that peat moss and oat hulls had the highest (0.68) and lowest (0.39) wall coefficient of friction, respectively. While, the adhesion coefficient values ranged from 0.2635 kPa for peat moss, to 16.203 kPa for flax shives.

Afzalinia and Roberge (2007) studied the static friction coefficient of alfalfa, barley straw, wheat straw and green barley on a polished steel surface at high pressure levels closer to baling or densification pressures, which were in the range of 200 to 735 kPa. The data revealed that the coefficient of friction of alfalfa and barley straw increased from 0.15 to 0.26 and 0.14 to 0.27 with an increase in material moisture content from 12.0 to 45.7% (wb), respectively. In addition, coefficients of friction for wheat straw at 10% moisture content and whole green barley at 51% moisture content were 0.13 and 0.21, respectively.

Fasina et al. (2006) determined the internal frictional and cohesion properties of peanut hull, switchgrass and poultry litter at hammer mill screen sizes of 0.79, 1.59 and 3.2 mm. They have determined that both peanut hull and switchgrass can be classified as cohesive materials while poultry litter can be classified as easy flowing material. In addition, the hammer mill screen size did not have any significant effect on the angle of internal friction and cohesive properties of

these materials. The average angle of internal friction for peanut hull, switchgrass and poultry litter were 42.82°±1.34, 41.76°±0.92, and 41.26°±1.43, respectively.

Chevanan et al. (2008) determined the frictional properties of chopped switchgrass (7.81 and 13.50 mm), wheat straw (7.09 and 10.39 mm) and corn stover (7.80 and 14.89 mm) using a direct shear cell at four applied normal stresses of 1.23, 2.46, 3.67 and 4.92 kPa. The chopped biomass coefficient of internal friction was in the range of 0.765 to 1.586 for the various normal pressures (Chevanan et al., 2008). The friction coefficient increased for reduced normal pressure for all three chopped biomass types, however, changing the particle size caused no statistically significant difference in the friction coefficients except at the lowest normal pressure of 1.23 kPa for chopped corn stover and chopped wheat straw.

Larsson (2010) determined the influence of normal stress on the coefficient of kinematic wall friction of reed canary grass powder from hammer mill screen size of 4.0 mm at low (0.52 to 7.52 kPa) and high (23 to 275 MPa) normal stresses. It was observed that at both low and high normal stresses, the coefficient of kinematic wall friction was negatively correlated to normal stress. However, high friction value of about 0.6 was observed for normal stress values of 50 MPa and lower. Hence, it was concluded that the friction values obtained probably originated from internal friction occurring within sample and not from kinematic wall friction.

The coefficient of internal friction has been reported by Fasina et al. (2006) for peanut hull, switchgrass and poultry litter, and Chevanan et al. (2008) for chopped switchgrass, wheat straw and corn stover. However, no studies were found on internal friction and cohesion properties of non-treated and steam exploded barley, canola, oat and wheat straw grinds. Therefore, the objective of the present study was to determine the effect of steam explosion pretreatment, hammer mill screen size, and normal forces on coefficient of internal friction and cohesion properties of non-treated and steam exploded barley, canola, oat and wheat straw.

3.3 Materials and Methods

3.3.1 Agricultural Biomass

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for the experiments. The straw samples were acquired in small square bale form (typically having dimensions of 0.45 x 0.35 x 1.00 m) during the summer of 2008 from a farmer in the Central Butte area of Saskatchewan, Canada.

The initial moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (wb), respectively. The agricultural biomass was stored under a tarpaulin cover during the winter of 2008 (approximately for 7 months). During this period the moisture content of barley, canola, oat and wheat straw increased to 13.5, 15.1, 13.1 and 15.6% (wb), respectively.

All of the baled straw samples were chopped using a chopper, which was fabricated in the Bioprocessing Lab, Department of Agricultural and Bioresource Engineering, University of Saskatchewan (Figure 2.1). The biomass chopper is a modified and compact version of the currently available New Holland Forage Chopper series 770 having similar specification of the chopper and cutter-bar. The biomass chopper was equipped with a feed hopper and a pair of rollers to feed the material to the chopping blades. The feed rate of biomass to the blades was dependent on the roller speed. After a few preliminary trials, the rollers were set to rotate at 50 rpm in order to avoid material clogging. Each of the six chopper blades were inclined at an angle of 14^{o} (with respect to horizontal axis of rotation) to deliver shearing effect on the biomass and were set to rotate at 460 rpm.

The chopped biomass was subsequently ground using a hammer mill (Serial no. 6M13688; 230 Brookdale, St. Maywood, NJ) with 22 swinging hammers having a peripheral velocity of 5.4 m/s, attached to a shaft powered by a 1.5 kW electric motor. Four screen sizes of 30, 6.4, 3.2 and 1.6 mm were used to grind the non-treated biomass. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK) having a 9 A suction fan rotating at 3500 rpm was connected to the outlet of the hammer mill to control dust during operation, provide flowability of chopped biomass through the hammer mill, and collect the ground biomass (Figure 2.2). A

portion (25 kg) of each of the biomass ground in the hammer mill using 30 mm screen was sent to FPInnovations in Quebec City, Quebec for steam explosion pretreatment.

3.3.2 Steam Explosion of Agricultural Biomass

The steam explosion of ground straw obtained using 30 mm hammer mill screen size was performed at the FPInnovations, Forintek pilot plant continuous steam explosion facility at Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized disc refiner having a plate gap of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive set to operate at 2000 rpm (Figure 3.1). The biomass flow through the refiner is wet (in suspension). The throughput of the equipment can vary between 50 and 200 kg of dried material per hour, depending on the bulk density of the raw material and the desired final particle size of the steam exploded material. The feed rate of agricultural straw into the digester was controlled using a plug screw feeder. The digester was operated at 180^{o}C (steam pressure of 900 kPa) for 4 min to perform steam explosion of the agricultural biomass. A flash tube convective dryer having 90 m long tube was used to dry the steam exploded barley, canola, oat and wheat straw at an average moisture content of 70.1, 80.7, 76.7 and 81.0% (wb) to approximately an average moisture content of 12.2, 13.6, 12.0 and 12.0% (wb), respectively. The direct heating of drying air was performed using 1172 kW (4 million BTU/h) natural gas burner, which has variable control to operate at different temperatures.

During the transportation of steam exploded material from Quebec City, Quebec to Saskatoon, Saskatchewan, the average moisture content of steam exploded barley, canola, oat and wheat straw was reduced to 7.8, 6.2, 6.8 and 7.0 % (wb), respectively. The steam exploded material was further ground in a hammer mill using three screen sizes of 6.4, 3.2 and 1.6 mm following the procedure described in the previous section. Figure 2.3 shows the photograph of non-treated (at hammer mill screen size of 30 mm) and steam exploded barley, canola, oat and wheat straw grinds.

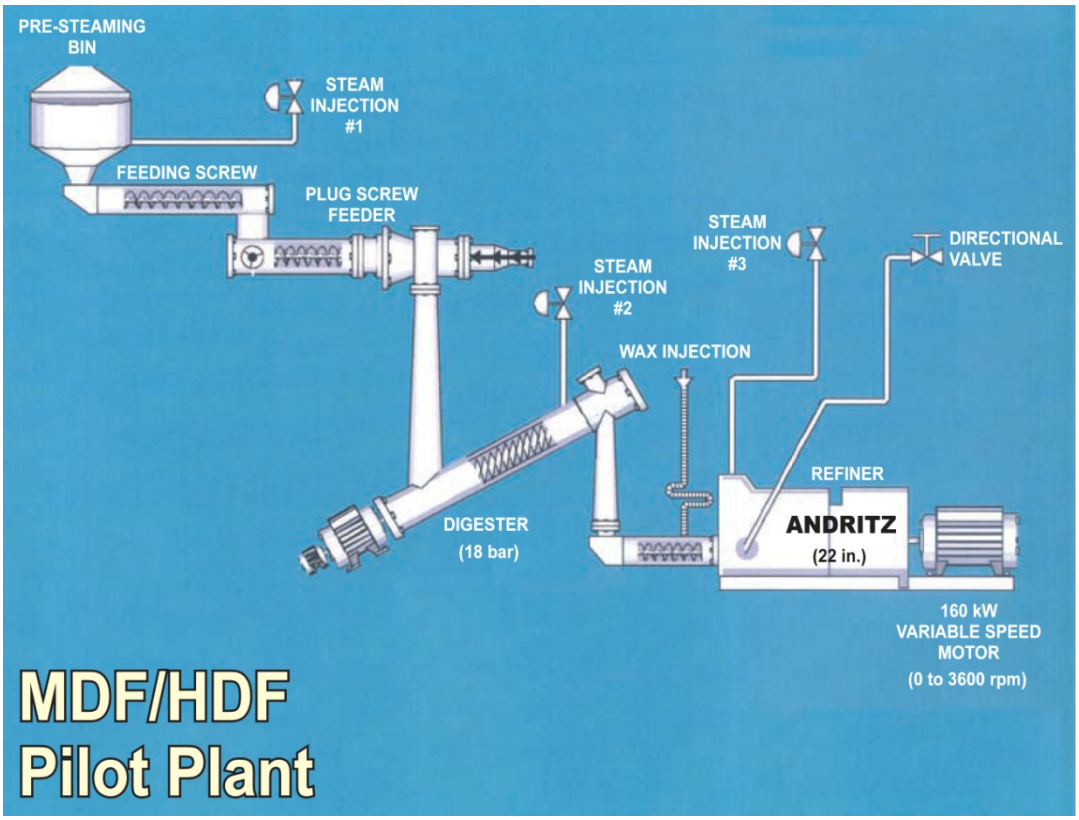


Figure 3.1: The Andritz (ANDRITZ AG, Graz, Austria) continuous biomass steam explosion facility for manufacturing of Medium Density and High Density Fiberboards (MDF/HDF), Forintek pilot plant at the FPInnovations, Quebec City, Quebec.

3.3.3 Moisture Content

The moisture content of baled straw and steam exploded biomass was determined using ASABE S358 (ASABE, 2006), where 25 g of material was oven-dried at 103^{o}C for 24 h. The moisture content of ground straw at hammer mill screen size of 6.4, 3.2 and 1.6 mm was determined using AACC Standard 44-15A (2005), where 2-3 g of material was oven-dried at 130^{o}C for 90 min. The resolution of weighing scale for mass measurement was up to three decimal places. Subsequently, the precision of moisture content was determined to two decimal places. All of the moisture content tests were performed in replicates of three.

3.3.4 Geometric Mean Particle Size

The geometric mean particle size of ground non-treated and steam exploded agricultural straw samples was determined using ASAE Standard S319 (2006b). Due to low bulk density of steam exploded straw, only 50 g of ground sample was placed on a stack of sieves arranged from the largest to the smallest opening. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used for particle size analysis. The sieve series selected were based on the range of particles in the samples. For grinds from 6.4 mm hammer mill screen opening, U.S. sieve numbers 10, 16, 20, 30, 50 and 70 (sieve opening sizes: 2.000, 1.190, 0.841, 0.595, 0.297 and 0.210 mm, respectively) were used. For grinds from 3.2 and 1.6 mm hammer mill screen openings, U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively) were used. A 10 min sieve shaking time was used as suggested in the ASAE Standard S319. The geometric mean size (d_{gw}) were calculated in replicates of three for each straw samples.

3.3.5 Bulk Density

Bulk density of hammer mill ground non-treated and steam exploded agricultural straw at three screen sizes of 6.4, 3.2 and 1.6 mm was determined by carefully filling a standard 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB) with sample. After filling every third portion of the container with ground straw sample, it was tapped on a wooden table for approximately 10 times to allow the material to settle down. After completely filling the container, excess material at the top was removed by moving a steel roller in a zig-zag pattern. The mass per unit volume gave the bulk density of the biomass in kg/m^3. Three replicates for each sample were performed for density measurements.

3.3.6 Experimental Setup and Procedure

The experimental set-up and procedures described in Mani et al. (2004) and Shaw and Tabil (2006) were adopted as a guideline for the present study in order to determine the coefficient of internal friction and cohesion. The Wykeham Farrance apparatus (Wykeham Farrance International Ltd., Slough, U.K.) (Mani et al., 2004; Shaw and Tabil, 2006; Afzalinai and Roberge, 2007) was used to perform the experiments on ground agricultural straw samples

(Figure 3.2). The apparatus consisted of a shear box for holding the biomass samples, a force transducer to record the frictional force, one linear variable differential transducers (LVDT) to measure the sample horizontal displacement, a linkage to apply the normal force to the sample, and an electrical motor to provide relative motion for the variable half of the sample box with respect to its fixed half. The dimensions of shear box were 100 mm square, 18 mm thick and 37 mm deep. Prior to the experiments, the agricultural straw was re-moistened to 10% moisture content (wb) by adding/sprinkling a calculated amount of water, except for canola and oat straw at 6.4 mm hammer mill screen size, which were already at 12.6 and 10.9% (wb), respectively. The samples were subsequently stored in plastic bags and kept in a cold room at 4^{o}C for a minimum of one week. Three levels of normal loads of 1.0, 2.0 and 4.0 kg (corresponding to 98.1, 196.2 and 392.4 N), with respective pressures of 9.8, 19.6 and 39.2 kPa were applied to the samples by weight acting through a load hanger that rested on the top plate. These loads were selected based on the studies performed by Shaw and Tabil [4], where high friction coefficients of around 0.6 were observed at normal stresses of 0.3 to 16.0 kPa for peat moss, wheat straw, oat hulls and flax shives. Larsson (2010) also showed that high friction coefficients of about 0.6 are observed below 50 MPa. In addition, Chevanan et al. (2008) also conducted their experiments at normal pressure of 1.23 to 4.92 kPa. The internal friction coefficient of ground straw sample was measured by filling the top and bottom halves of the box. Subsequently, the bottom half of the box was pulled at a constant speed of 1.2 mm/min in the horizontal direction to apply the shear force at three levels of normal loads. A total of three replicates were performed for each biomass sample and individual normal loads. The maximum shear stresses were plotted versus the normal pressures (normal stress) for non-treated and steam exploded barley, canola, oat and wheat straw at three hammer mill grinds sizes. The coefficient of internal friction was calculated from equation (1) as the slope of the relationship. The cohesion (*C*) was calculated as the intercept defined by the Mohr-Coulomb model (Chung and Verma, 1989):

$$\tau = \mu\sigma + C \tag{1}$$

where, τ is shear stress (kPa), σ is normal stress (kPa), μ is the coefficient of internal friction, and C is the cohesion (kPa).

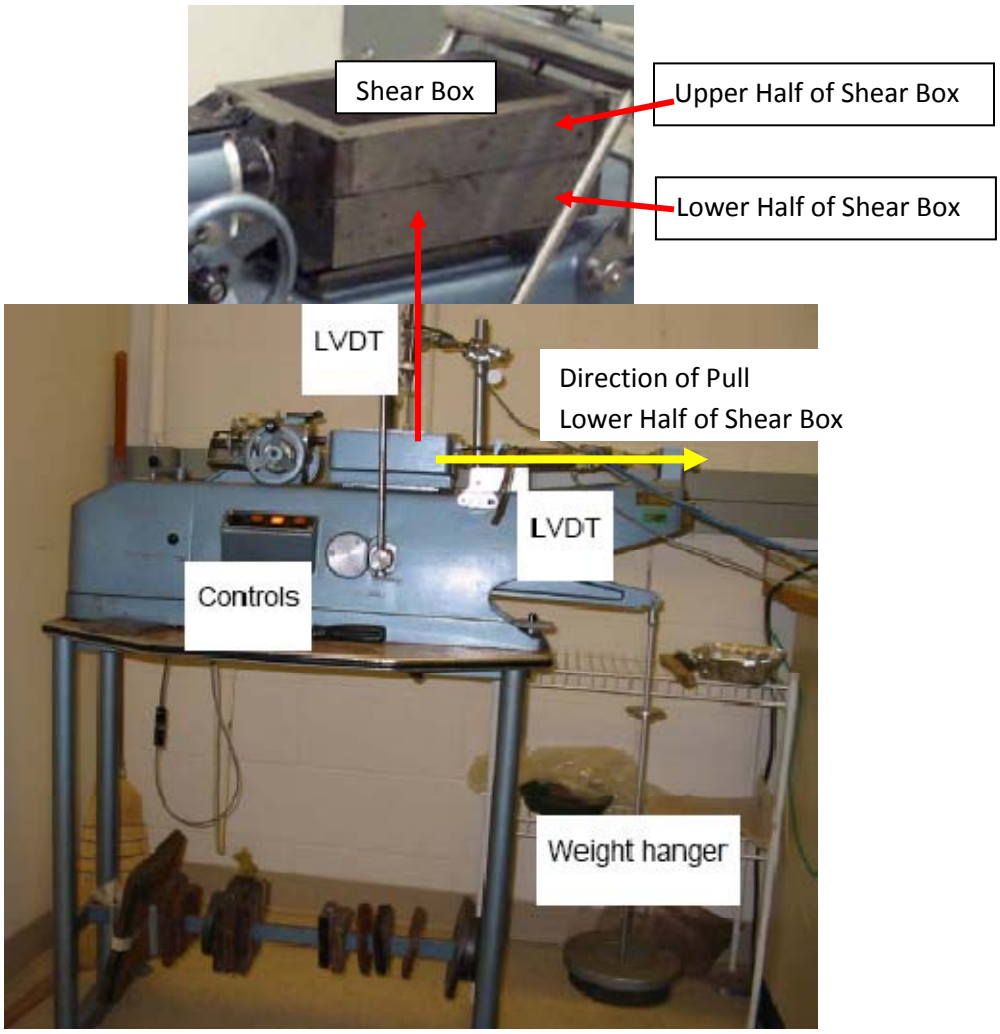


Figure 3.2: The Wykeham Farrance shear cell used to measure the coefficients of internal friction and cohesion for non-treated and steam exploded barley, canola, oat and wheat straw grinds.

3.3.7 Statistical Analysis

The experiments were set up as completely random experimental design with 3 replications of shearing stress (to determine internal friction and cohesion) and four-variable (straw, pre-treatment, hammer mill screen size and normal load) factorial design. Coefficient of internal friction and cohesion were the dependent variables, while straw, pre-treatment, hammer mill screen size and normal load were the independent variables. Statistical analyses were conducted on the geometric mean particle size, bulk density and shear stress data using SAS for Windows

(version 8.2) (SAS, 1999). The SAS general linear model (GLM) for completely randomized design (CRD) procedure was used and the Student-Neuman-Keuls test (SNK) was performed to determine the difference between any two treatment means at 5% level of significance (SAS Manual, 1999). Best predictor equations were developed for coefficient of internal friction and cohesion having the highest coefficient of determination (R^2) with straw, pre-treatment, hammer mill screen size and normal pressure being the independent variables. The equation parameters were estimated using Microsoft Excel software for Windows (version 8.2).

In addition, test of normality for particle size distribution (percentage mass of grinds retained over the sieves using ASAE Standard S319 (ASABE, 2006b) of non-treated and steam exploded grinds obtained from hammer mill screen sizes of 6.4, 3.2 and 1.6 mm were performed using Proc Univariate Normal Plot analysis in SAS (1999). The analysis of the mass retained on the sieves was performed using three methods, namely: Shapiro-Wilk test, and determination of skewness and kurtosis values. The Shapiro-Wilk statistic (W) can be used to test if the observations follow a normal distribution and the probability (P value) is used to accept or reject the hypothesis of whether the data is normally distributed or not. The data is normally distributed if $P > 0.05$. Skewness and Kurtosis are two measures of departure from a normal distribution; both statistics will be equal to zero if the data is normally distributed.

3.4 Results and Discussion

3.4.1 Geometric Mean Particle Size and Distribution

Table 3.1 shows the mean geometric particle sizes for non-treated and steam exploded barley, canola, oat and wheat straw. The mean geometric particle size for any particular biomass decreased with a decrease in hammer mill screen size from 6.4 to 1.6 mm. The decrease in mean particle diameter was significant for non-treated canola and wheat straw, and steam exploded barley, oat and wheat straw; however, non-treated barley and oat straw, and steam exploded canola straw at hammer mill screen sizes of 3.2 and 1.6 mm did not show a significant change.

The geometric mean particle size of steam exploded straw at any specific hammer mill screen size was significantly smaller than that of the non-treated straw. This could be due to the fact

that application of steam explosion pre-treatment disintegrates the lignocellulosic structure of the biomass (Sokhansanj et al., 2005) leading to lower shear strength (easier to grind the straw).

Table 3.1: Feed rate, Moisture content, geometric mean particle size and bulk density for non-treated and steam exploded barley, canola, oat and wheat straw samples.

Agricultural Biomass	Hammer Mill Screen Size (mm)	Hammer Mill Feed Rate (kg/h)	Moisture Content Post-Grinding (%, wb)	Geometric Mean Particle Size (mm)*	Bulk Density (kg/m^3)*
Non-Treated Straw					
Barley Straw	6.4	74	8.9±0.4‡†	0.883±0.025 aDX£	96±02 aDX
	3.2	63	5.3±0.3	0.463±0.016 bDX	149±03 bDEX
	1.6	25	7.8±0.2	0.456±0.004 bDX	155±01 cDX
Canola Straw	6.4	67	12.6±0.2	0.885±0.020 aDX	144±02 aEX
	3.2	46	9.2±0.1	0.521±0.061 bDEX	190±09 bFX
	1.6	38	8.3±0.2	0.367±0.001 cEX	203±11 bEX
Oat Straw	6.4	88	10.9±0.1	0.935±0.013 aDX	111±08 aFX
	3.2	53	9.4±0.3	0.566±0.015 bEX	156±04 bDX
	1.6	24	7.7±0.1	0.404±0.014 bFX	196±04 cEX
Wheat Straw	6.4	90	9.5±0.4	0.997±0.038 aEX	107±02 aFX
	3.2	44	9.5±0.3	0.719±0.015 bFX	141±02 bEX
	1.6	25	8.6±0.3	0.452±0.016 cDX	154±02 cDX
Steam Exploded Straw					
Barley Straw	6.4	49	5.8±0.3	0.607±0.028 aDY£	38±03 aDY
	3.2	43	4.8±0.2	0.368±0.002 bDY	73±02 bDY
	1.6	32	4.6±1.2	0.296±0.013 cDY	93±06 cDY
Canola Straw	6.4	64	4.3±0.0	0.698±0.127 aDY	33±02 aEY
	3.2	50	4.2±0.1	0.447±0.010 bEY	44±00 bEY
	1.6	35	4.6±0.1	0.364±0.007 bEY	67±02 cEY
Oat Straw	6.4	60	4.6±0.2	0.602±0.012 aDY	43±01 aFY
	3.2	46	4.5±0.1	0.367±0.010 bDY	77±04 bDY
	1.6	31	4.1±0.2	0.327±0.022 cDY	91±03 cDY
Wheat Straw	6.4	52	4.5±0.2	0.568±0.10 aDY	41±01 aDFY
	3.2	45	4.7±0.4	0.387±0.005 bFY	73±05 bDY
	1.6	35	4.3±0.3	0.309±0.012 cDY	100±05 cDY

*bulk density and geometric mean particle size have been measured at 10% moisture content

‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass at various hammer mill screen sizes (a, b and c); at same hammer mill screen sizes for different sample biomass (D, E and F); for any particular biomass at same hammer mill screen size for non-treated and steam exploded biomass (X and Y)

Table 2.2 and Figure 2.4 represents the measure of particle size distribution of selected biomass grinds obtained from hammer mill using three different screen sizes of 6.4, 3.2 and 1.6 mm. Using the Shapiro-Wilk test, it has been determined that the non-treated barley and wheat straw grinds obtained from 6.4 mm screen hammer mill are not normally distributed ($P < 0.05$), skewed towards right (positive values) and higher peaks than expected for the normal distribution (positive value). Mani et al. (2004) reported that wider particle size distribution is suitable for compaction (pelleting/briquetting) process. During compaction, smaller (fine) particles rearrange and fill in the void space of larger (coarse) particles producing denser and durable compacts (Tabil, 1996). Therefore, ideally the grinds should be normally distributed (Shapiro-Wilk test: $P > 0.05$), should have near zero skewness and lower peak than expected for the normal and wider distribution of data (negative Kurtosis values). Upon application of this concept on Table 2, it can be deduced that for non-treated barley straw at 1.6 mm hammer mill screen size ($P > 0.05$; Skewness = 0.276; Kurtosis = -1.875), canola straw ($P > 0.05$; Skewness = 0.039; Kurtosis = -2.774), oat straw ($P > 0.05$; Skewness = -0.080; Kurtosis = -2.912), and wheat straw ($P > 0.05$; Skewness = 0.554; Kurtosis = -1.862) at 3.2 mm hammer mill screen size resulted in grinds that would potentially produce better compacts. For steam exploded agricultural biomass, Table 2 also shows that barley ($P > 0.05$; Skewness = -0.097; Kurtosis = -1.077), canola ($P > 0.05$; Skewness = -0.202; Kurtosis = -2.725) and wheat ($P > 0.05$; Skewness = 0.652; Kurtosis = 0.044) straw at 6.4 mm hammer mill screen size, and oat ($P > 0.05$; Skewness = 0.088; Kurtosis = -1.272) straw at 1.6 mm screen size would potentially produce better compacts.

3.4.2 Bulk Density

The bulk density values for barley, canola, oat and wheat straw grinds are given in Table 3.1. The bulk density of non-treated and steam exploded straw significantly increased with a decrease in hammer mill screen size from 6.4 to 1.6 mm, except for non-treated canola straw at 3.2 and 1.6 mm.

The bulk density of non-treated barley, canola, oat and wheat straw at any specific hammer mill screen size was significantly higher than steam exploded straw (Table 3.1). This could again be attributed to the fact that application of steam explosion pre-treatment disintegrates the organized and compact lignocellulosic structure of biomass leading to lower bulk densities.

3.4.3 Frictional Properties

Tables 3.2-3.5 show that predominantly a linear correlation exists (higher R^2 values) between normal and shear stress for non-treated and steam exploded barley, canola, oat and wheat straw grinds. In addition, it has been observed that the shear stress for both non-treated and steam exploded straw at any specific hammer mill screen size significantly increased with an increase in normal stress. It is typically expected that the shear stress should be lower than normal stress. Most of the measured data points in this study show this trend, but some data show the opposite. Similar observations were made by Chevanan et al. (2008) for chopped switchgrass, wheat straw and corn stover, and by Richter (1954) for chopped grass and corn silage, where higher shear stress than normal stress values were observed. This phenomenon was usually observed at lower applied pressures, with a few exceptions at higher pressures, primarily due to fibrous and irregular shaped particles.

The shear stress for non-treated and steam exploded barley, canola and wheat straw at any specific normal stress was not significantly different at various hammer mill screen sizes, with a few exceptions for steam exploded straw (Table 3.2, 3.3 and 3.5). As a result, the sum of square of error (SSE) values had higher degree of variability in steam exploded material as compared to non-treated straw (Table 3.2, 3.3 and 3.5).

At any specific normal stress, the shear stress was not significantly different at 3.2 and 1.6 mm screen size for non-treated oat straw. In general, the shear stress for non-treated and steam exploded oat straw grinds at 6.4 mm screen size was significantly lower than 3.2 and 1.6 mm screen size at all normal stress, with a few exceptions (Table 3.4). No specific trend was observed for steam exploded material (Table 3.4).

In general, the shear stress values for steam exploded barley, oat and wheat straw grind at all hammer mill screen sizes and normal stress were significantly higher than those of the non-treated straw (Tables 3.2, 3.4 and 3.5). This could be due to significantly lower bulk densities of steam exploded material as compared to non-treated material. It can also be confirmed from the fact that highly compressible powders (lower bulk density) are less flowable, and vice versa (Mani et al., 2004). As a result, the coefficient of internal friction was higher for steam exploded straw as compared to non-treated straw.

The shear stress values for non-treated and steam exploded canola straw were not significantly different, except for steam exploded straw at 6.4 mm screen size and 39.2 kPa normal stress, and screen sizes of 3.2 mm and 1.6 mm at 9.8 kPa normal stress, which were significantly higher (Table 3.3). The result for canola straw has been in contrary to those observed for barley, oat and wheat straw. Therefore, it has been realized that the shear stress values could be a result of a combination of different factors. Table 3.1 depicts that the geometric mean particle sizes for steam exploded canola straw is significantly higher than non-treated straw; however, the increase in values at different hammer mill screen size is lower than other straws. Therefore, it is anticipated that a combination of bulk density and geometric mean particle diameter of the canola straw resulted in insignificant differences in shear stress values. However, the coefficient of internal friction was higher for steam exploded straw as compared to non-treated straw.

The coefficient of internal friction obtained for non-treated and steam exploded barley, canola, oat and wheat straw grinds at average geometric mean particle sizes from Tables 3.2-3.5 were plotted in Figure 3.3. Power, logarithmic or exponential equations having the highest R^2 values have been fitted to the experimental data. These equations can be used to predict the coefficient of internal friction (slope of the linear plot) for various hammer mill screen sizes. In general, the coefficient of internal friction for non-treated straw decreased with an increase in average geometric mean particle diameter. Highest coefficient of friction was observed for canola straw grinds. The coefficient of friction for steam exploded barley, canola and wheat decreased and for steam exploded oat it increased with an increase in geometric mean particle diameter.

Shaw and Tabil (2006) reported a wall friction coefficient of 0.45 (geometric mean particle diameter of 0.65 mm) for wheat straw grinds on a mild steel surface, compared to the value of 0.59 (coefficient of internal friction) (geometric mean particle diameter of 0.72 mm) obtained from this study. Similarly, Mani et al. (2004) reported wall friction coefficients of 0.18 and 0.19 for corn stover grinds obtained from hammer mill screen sizes of 6.4 and 3.2 mm, respectively, which are again significantly, lower than values observed in the present study. Therefore, higher friction values are encountered when biomass grind particles are sheared against other particles of the same biomass grinds (coefficient of internal friction) as opposed to sheared against mild steel surface (wall friction coefficient). Afzalinia and Roberge (2008) reported mean internal friction coefficients of 0.44 and 0.30 for alfalfa (10 mm chop length) and barley straw (19 mm

chop length) at 12% moisture content, respectively, which are significantly lower than obtained for barley grinds. However, it should be noted that Afzalinia and Roberge (2008) obtained these values at high pressure levels closer to baling or densification pressures, which were in the range of 200 to 735 kPa. Lower internal friction values could be due a combination of both higher normal pressures (Tabil and Sokhansanj, 1997) and chop lengths.

The cohesion for non-treated and steam exploded barley, canola, oat and wheat straw grinds at average geometric mean particle sizes from Tables 3.2-3.5 are plotted in Figure 3.4. Mostly, power, logarithmic or exponential equations having the highest R^2 values have been fitted to the experimental data. These equations can be used to predict the cohesion (intercept of the linear plot) for various geometric mean particle sizes. The coefficient of cohesion for non-treated barley, canola, oat and wheat straw increased with an increase in average geometric mean particle diameter. The coefficient of cohesion for steam exploded barley and wheat straw increased and for steam exploded canola and oat straw decreased with an increase in average geometric mean particle diameter.

Table 3.2: Normal stress (σ), shear stress (τ), coefficient of internal friction (μ) and cohesion (*C*) of non-treated and steam exploded barley grinds at 10% moisture content (wb).

Barley Straw	Hammer Mill Screen Sizes (mm)	σ (kPa)	τ (kPa)	μ	*C* (kPa)	R^2	SSE*
Non-Treated	6.4	9.8	9.95±0.48‡† aDX£	0.505	5.394	0.98	0.937
		19.6	15.92±0.53 bDX				1.694
		39.2	25.02±1.38 cDX				3.900
	3.2	9.8	10.18±0.35 aDX	0.584	4.782	0.99	0.580
		19.6	16.76±0.23 bDX				0.910
		39.2	27.55±0.80 cDX				1.333
	1.6	9.8	10.48±0.74 aDX	0.562	4.935	0.98	1.093
		19.6	15.92±0.93 bDX				1.728
		39.2	27.01±1.53 cDX				4.674
Steam Exploded	6.4	9.8	13.70±0.93 aDY	0.562	8.149	0.98	1.725
		19.6	19.13±0.48 bDY				0.463
		39.2	30.23±1.78 cDY				6.361
	3.2	9.8	12.17±0.23 aEY	0.723	4.706	0.98	0.512
		19.6	18.37±0.83 bDY				2.201
		39.2	33.29±2.21 cDEY				9.934
	1.6	9.8	13.62±0.13 aDY	0.738	6.657	1.00	0.264
		19.6	21.58±0.61 bEY				1.324
		39.2	35.51±0.53 cEY				0.599

‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample hammer mill screen size at various normal stress (a, b and c); at same normal stress for different hammer mill screen sizes (D, E and F); at same hammer mill screen size and normal stress for non-treated and steam exploded straw (X and Y); *SSE – Sum Square of Errors for predicted and experimental shear stress values

Table 3.3: Normal stress (σ), shear stress (τ), coefficient of internal friction (μ) and cohesion (*C*) of non-treated and steam exploded canola grinds at 10% moisture content (wb).

Canola Straw	Hammer Mill Screen Sizes (mm)	σ (kPa)	τ (kPa)	μ	*C* (kPa)	R^2	SSE*
Non-Treated	6.4	9.8	12.47±0.58‡† aDX£	0.665	6.083	1.00	0.721
		19.6	19.36±0.74 bDX				1.247
		39.2	32.14±0.23 cDX				0.110
	3.2	9.8	12.24±0.13 aDX	0.661	5.853	0.99	0.062
		19.6	18.98±0.70 bDX				1.056
		39.2	31.76±1.16 cDX				2.673
	1.6	9.8	12.32±0.87 aDX	0.663	5.624	1.00	1.621
		19.6	18.37±0.00 bDX				0.214
		39.2	31.76±0.58 cDX				0.708
Steam Exploded	6.4	9.8	11.33±0.27 aDX	0.739	3.864	0.98	0.275
		19.6	18.06±0.93 bDX				2.000
		39.2	32.98±2.77 cDY				15.360
	3.2	9.8	12.55±0.27 aEY	0.708	5.509	0.99	0.168
		19.6	19.28±0.46 bDX				0.462
		39.2	33.36±1.53 cDX				4.688
	1.6	9.8	13.62±0.35 aFY	0.841	5.700	1.00	0.572
		19.6	22.73±0.61 bEX				1.569
		39.2	38.57±0.83 cEX				1.424

‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample hammer mill screen size at various normal stress (a, b and c); at same normal stress for different hammer mill screen sizes (D, E and F); at same hammer mill screen size and normal stress for non-treated and steam exploded straw (X and Y); *SSE – Sum Square of Errors for predicted and experimental shear stress values

Table 3.4: Normal stress (σ), shear stress (τ), coefficient of internal friction (μ) and cohesion (*C*) of non-treated and steam exploded oat grinds at 10% moisture content (wb).

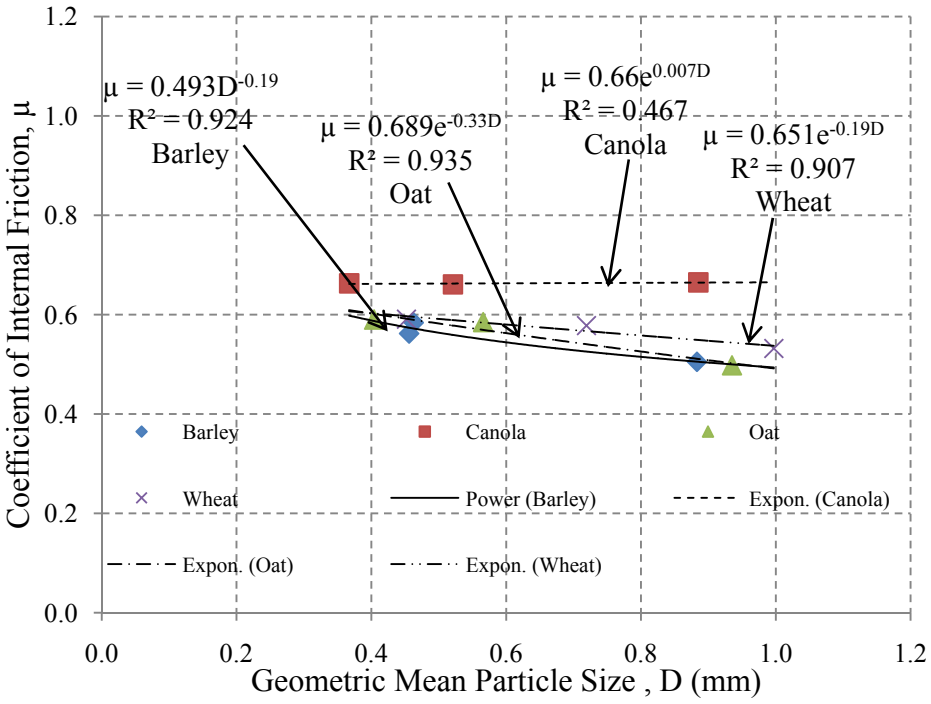
Oat Straw	Hammer Mill Screen Sizes (mm)	σ (kPa)	τ (kPa)	μ	*C* (kPa)	R^2	SSE*
Non-Treated	6.4	9.8	9.87±0.23‡† aDX£	0.498	5.050	0.99	0.118
		19.6	14.92±0.92 bDX				1.717
		39.2	24.56±0.92 cDX				1.689
	3.2	9.8	10.33±0.40 aDEX	0.585	4.553	1.00	0.321
		19.6	15.99±0.48 bDEX				0.461
		39.2	27.55±0.61 cEX				0.742
	1.6	9.8	10.94±0.48 aEX	0.590	5.165	0.99	0.457
		19.6	16.76±0.46 bEX				0.422
		39.2	28.31±1.18 cEX				2.776
Steam Exploded	6.4	9.8	11.78±0.70 aDY	0.860	1.836	0.92	7.839
		19.6	16.45±0.13 bDY				15.320
		39.2	36.35±5.51 cDY				62.501
	3.2	9.8	13.16±0.48 aEY	0.660	6.810	0.97	0.502
		19.6	19.97±0.46 bEY				0.557
		39.2	32.67±2.91 cDY				16.902
	1.6	9.8	13.62±0.13 aEY	0.745	6.810	0.97	0.778
		19.6	22.19±0.70 bFY				2.736
		39.2	35.81±3.09 cDY				19.239

‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample hammer mill screen size at various normal stress (a, b and c); at same normal stress for different hammer mill screen sizes (D, E and F); at same hammer mill screen size and normal stress for non-treated and steam exploded straw (X and Y); *SSE – Sum Square of Errors for predicted and experimental shear stress values

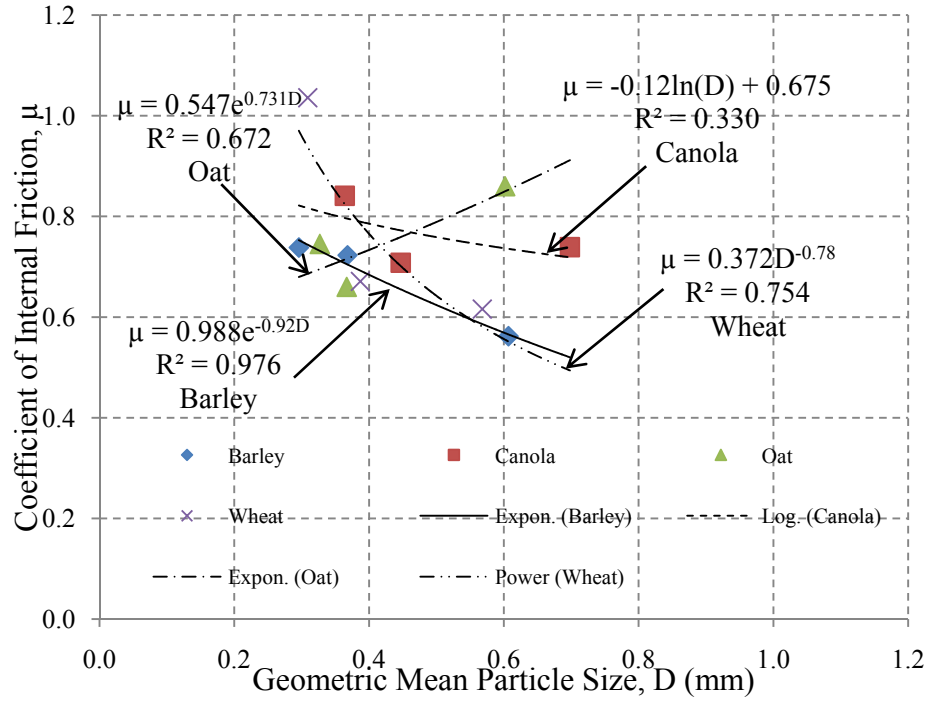
Table 3.5: Normal stress (σ), shear stress (τ), coefficient of internal friction (μ) and cohesion (*C*) of non-treated and steam exploded wheat grinds at 10% moisture content (wb).

Wheat Straw	Hammer Mill Screen Sizes (mm)	σ (kPa)	τ (kPa)	μ	*C* (kPa)	R^2	SSE*
Non-Treated	6.4	9.8	10.48±0.48‡† aDX£	0.532	5.586	0.99	0.767
		19.6	16.53±0.83 bDX				2.134
		39.2	26.32±0.87 cDX				1.568
	3.2	9.8	10.87±0.13 aDX	0.578	5.394	0.99	0.153
		19.6	17.06±0.48 bDX				0.783
		39.2	28.01±0.83 cDX				1.384
	1.6	9.8	10.64±0.74 aDX	0.591	5.088	0.99	1.276
		19.6	17.06±0.53 bDX				0.997
		39.2	28.16±1.04 cDX				2.186
Steam Exploded	6.4	9.8	11.40±0.35 aDEY	0.616	5.624	1.00	0.457
		19.6	18.14±0.23 bDX				0.649
		39.2	29.69±0.48 cDX				0.490
	3.2	9.8	10.18±0.66 aDY	0.671	4.132	0.95	1.744
		19.6	18.14±3.59 bDX				27.826
		39.2	30.23±0.87 cDY				1.678
	1.6	9.8	12.63±0.83 aEY	1.036	1.568	0.99	3.772
		19.6	20.58±1.46 bDY				9.401
		39.2	42.70±0.46 cEY				1.107

‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample hammer mill screen size at various normal stress (a, b and c); at same normal stress for different hammer mill screen sizes (D, E and F); at same hammer mill screen size and normal stress for non-treated and steam exploded straw (X and Y); *SSE – Sum Square of Errors for predicted and experimental shear stress values

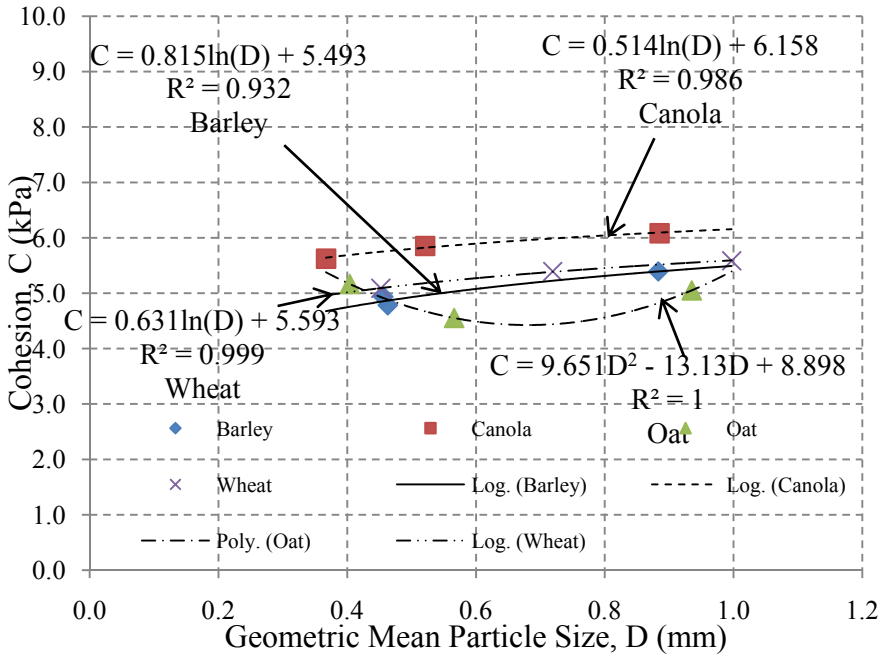


(a) Non-Treated Straw

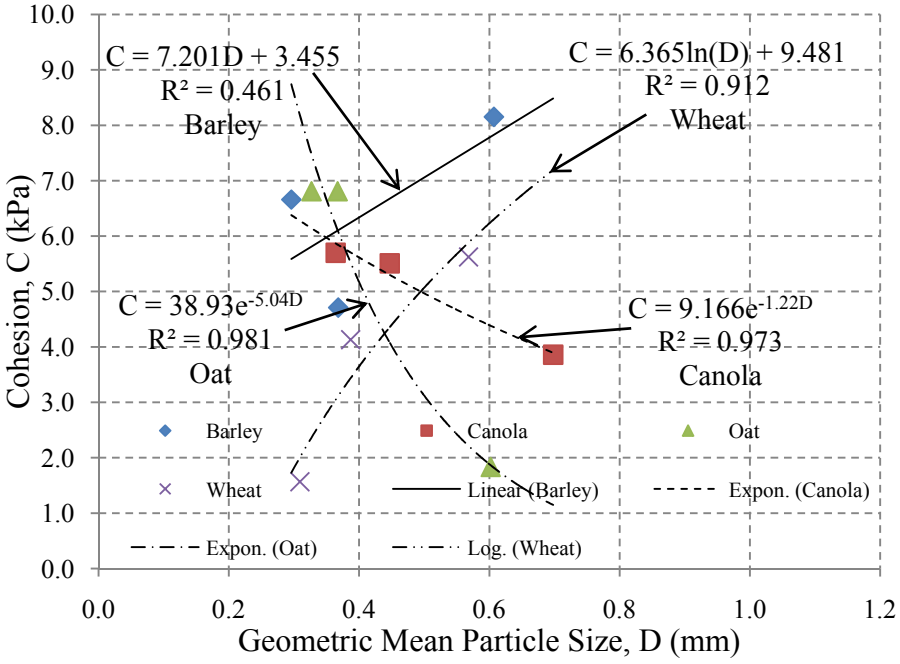


(b) Steam Exploded Straw

Figure 3.3: Relationship between coefficient of internal friction (μ) and geometric mean particle sizes (D) for non-treated and steam exploded barley, canola, oat and wheat straw grinds at 10% moisture content (wb).



(a) Non-Treated Straw



(b) Steam Exploded Straw

Figure 3.4: Relationship between cohesion coefficient (*C*) and geometric mean particle sizes (D) for non-treated and steam exploded barley, canola, oat and wheat straw grinds at 10% moisture content (wb).

3.5 Conclusions

The following conclusions could be derived from this study:

1. An increase in normal stress from 9.8 kPa to 39.2 kPa significantly increased the shear stress values for non-treated and steam exploded straw.

2. In general, hammer mill screen size (1.6 mm, 3.2 mm and 6.4 mm) did not have any significant effect on shear stress values for non-treated and steam exploded straw.

3. The steam exploded straw grinds resulted in higher coefficient of internal friction compared to non-treated straw grinds primarily because of lower bulk densities.

4. Equations were developed to predict coefficient of internal friction and cohesion with respect to hammer mill screen sizes for non-treated and steam exploded barley, canola, oat and wheat straw grinds.

Chapter 4

4. Quantitative Analysis of Lignocellulosic Components of Agricultural Straw Using Fourier Transform Infrared Spectroscopy

A similar version of the first half of this chapter (section 4.2) has been published in the CIGR Ejournal. This journal article provides a detailed description of the lignocellulosic structure and explores the principles of application of infrared spectroscopy to determine lignocellulosic composition:

- Adapa, P.K., C. Karunakaran, L.G. Tabil and G.J. Schoenau. 2009. Potential applications of infrared and Raman spectromicroscopy for agricultural biomass. *Agricultural Engineering International: the CIGR Ejournal*, Manuscript 1081, XI(February): 1-25.

A similar version of the second half of this chapter (section 4.3) has been published in the Journal of Agricultural Science and Technology. A novel procedure was established and regression equations have been developed to perform qualitative and quantitative analysis in this journal article:

- Adapa, P.K., L.G. Tabil, G.J. Schoenau, T. Canam, and T. Dumonceaux. 2011. Quantitative analysis of lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat straw using Fourier transform infrared spectroscopy. *Journal of Agricultural Science and Technology*, B1(2011): 177-188.

During the course of development and refining of the experimental procedure, three papers were presented and published in national and international conferences. Preliminary findings are presented in Appendix A, which is based on peak height from single characteristic wavenumber for cellulose, hemicelluloses and lignin, and also for one replication:

- Adapa, P.K., C. Karunakaran, L.G. Tabil and G.J. Schoenau. 2008. Application of FT-IR and FT-Raman spectromicroscopy to study chemical compound characterization and distribution in agricultural biomass - a review. CSBE/ASABE Red River Inter-sectional Meeting at Hotel Holiday Inn, Winnipeg, Manitoba, Paper No. RRV 08-603, Sept. 19-20. St. Joseph, MI: ASABE.
- Adapa, P.K., C. Karunakaran, L.G. Tabil and G.J. Schoenau. 2009. Qualitative and quantitative analysis of lignocellulosic biomass using infrared spectroscopy. CSBE/SCGAB Annual General Meeting and Technical Conference, Prince Edward Island, Paper No. CSBE09307, July 12-15: CSBE.
- Adapa, P.K., L.G. Tabil, G.J. Schoenau, T. Canam, M. Gruber and T. Dumonceaux. 2010. Application of infrared spectromicroscopy to characterize and determine lignocellulosic components in agricultural straw. CSBE/SCGAB the 17th World Congress of the International Commission of Agricultural Engineering (CIGR), Quebec City, Quebec, Paper No. CSBE100647, June 13-17: CSBE

Contributions of Ph.D. Candidate

A review of the structural and chemical characteristics of agricultural biomass was successfully performed, which explored the basic concepts of Infrared Spectroscopy, and evaluated its strengths and drawbacks as applied to lignocellulosic biomass. This review was critical since no such studies have been conducted to assess the potential of infrared spectroscopy, and determine the structural characteristics and chemical components distribution in agricultural biomass using Infrared Spectroscopy enabling it suitable for biorefineries. Subsequently, a novel procedure to rapidly quantify the lignocellulosic composition of non-treated and steam exploded barley, canola, oat and wheat straw was developed, which could be easily extended for any form of

lignocellulosic biomass using Fourier Transform Infrared (FTIR) spectroscopy. Literature review, experiments, data analysis and manuscript writing were performed by Phani Adapa, while Dr. Lope Tabil and Dr. Greg Schoenau provided input in terms of the conduct of experiment, analysis of the results and editing of the manuscript. Dr. Chithra Karunakaran provided guidance in structuring the review article and designing of preliminary FTIR experiments at the Canadian Light Source (Synchrotron), while Dr. Thomas Canam, Dr. Margie Gruber and Dr. Tim Dumonceaux provided lab-based experimental data on lignocellulosic composition of agricultural biomass.

Contribution of these Papers to Overall Study

Knowledge Gap: In literature, no studies have been conducted to perform qualitative and quantitative analysis of agricultural (lignocellulosic) biomass to determine change in cellulose-hemicellulose-lignin composition prior to and after application of various pre-processing and pre-treatment methods. Therefore, the objectives were: a) to review the structural and chemical characteristics of agriculture-based lignocellulosic biomass, and also review the concepts and application of IR and Raman spectromicroscopy methods for biomass research; and b) to estimate critical parameters in analytical specification of lignocellulosic biomass and consequently, develop and validate a rapid method for the qualitative and quantitative analysis of cellulose-hemicellulose-lignin composition of non-treated and steam exploded barley, canola, oat and wheat straw using Fourier Transform Infrared Spectroscopy (FTIR).

Justification: The effect of various pre-processing and pre-treatment methods on the lignocellulosic matrix at the molecular level is not well understood. Applications of pre-processing methods such as size reduction or increasing porosity, and pre-treatment techniques such as steam explosion on agricultural biomass have demonstrated an improvement in pellet (compact) quality that can be attributed to the changes in the lignocellulosic components and distribution (Bagby, 1982; Focher et al., 1998). Therefore, it is critical to rapidly quantify the change in cellulose, hemicelluloses and lignin components of biomass due to application of pre-treatment methods.

Infrared spectroscopy has the potential to produce qualitative and quantitative analytical data for samples with minimum or no sample preparation, and at high speed and throughput (Budevska, 2002; Luypaert et al., 2003; Smola and Urleb, 2000; Tucker et al., 2000). Traditionally, chemical analyses of the individual components (e.g., lignin) of lignocellulosics have been performed by acid hydrolysis followed by gravimetric determination of lignin (Kelley et al., 2004). These methods can provide highly precise data. However, these methods are laborious, time-consuming, and, consequently, expensive to perform and sample throughput is limited.

4.1 Abstract

The low bulk density agricultural biomass should be processed and densified making it suitable for biorefineries. However, many agricultural biomass (lignocellulosic) especially those from straw and stover results in poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture. The binding characteristics of biomass can be enhanced by modifying the structure of lignocellulose matrix (cellulose-hemicellulose-lignin) by different pre-processing and pre-treatment methods. However, it is not well understood as to how various pre-processing and pre-treatment methods affect the lignocellulosic matrix at the molecular level. Therefore, it is essential to determine chemical composition of agricultural biomass and the distribution of lignin relative to cellulose and hemicellulose before and after application of various treatment methods and after densification process. In the first journal article, the structural characteristics of lignocellulosic plant biomass and applications of Infrared (IR) and Raman spectromicroscopy methods are reviewed. The IR and Raman methods have good potential to determine the structural characteristics and chemical components distribution in lignocellulosic biomass. Both these methods have their own advantages and drawbacks, and should be used as complementary techniques.

The second article addressed the issue of rapid and cost effective quantification of lignocellulosic components (cellulose, hemicelluloses and lignin) of agricultural biomass (barley, canola, oat and wheat) to determine the effect of various pre-treatments (such as steam explosion) on biomass used as feedstock for the biofuel industry. Fourier Transformed Infrared (FTIR) spectroscopy was considered as an option to achieve this objective. Regression equations having

R^2 values of 0.89, 0.99 and 0.98 were developed to predict the cellulose, hemicelluloses and lignin compounds of biomass, respectively. The average absolute difference in predicted and measured cellulose, hemicellulose and lignin in agricultural biomass was 7.5%, 2.5%, and 3.8%, respectively.

4.2 Potential Applications of Infrared and Raman Spectroscopy for Agricultural Biomass

4.2.1 Introduction

Agricultural biomass residues have the potential for the sustainable production of bio-fuels and to offset greenhouse gas emissions (Campbell et al., 2002; Sokhansanj et al., 2006). The straw and agricultural residues existing in the waste streams from commercial crop processing plants have little inherent value and have traditionally constituted a disposal problem. In fact, these residues represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass (Liu et al., 2005). New methodologies need to be developed to process the biomass making it suitable feedstock for bio-fuel production. In addition, some of the barriers to the economic use of agricultural crop residue are uncertainty in its availability, variablility in quality, cost of collection, problems in transportation and storage (Bowyer and Stockmann, 2001; Sokhansanj et al., 2006).

Biomass must be processed and handled in an efficient manner in order to reduce industry's operational cost as well as to meet the requirement of raw material for biofuel production. Biomass has low bulk density, making it difficult and expensive to store and transport in its native loose form. The bulk density of dried alfalfa straw is as low as 40 kg/m^3. The bulk density of pelleted forage can be as high as 1250 kg/m^3 (Adapa et al., 2002). When densified, many agricultural biomass especially those from straw and stover result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture. This is a result of lack of complete understanding on the binding characteristics of the components that make up biomass (Sokhansanj et al., 2005).

The binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-

treatment methods (Sokhansanj et al., 2005). However, it is not well understood on how various pre-processing and pre-treatment methods affect the lignocellulosic matrix at the molecular level. Most studies focussed on quantification of chemical composition of biomass such as total energy content, crude protein and carbohydrates (structural and non-structural) using traditional chemical or proximate analysis methods (Adapa et al., 2004). The proximate analysis of lignocellulosic material relies on the separation of the component of interest from the complex matrix that makes up the biomass. As a result, information on the spatial origin and distribution of the component of interest is lost and the object of the analysis is destroyed (Budevska, 2002; Yu et al., 2007). In addition, applications of pre-processing methods such as size reduction or increasing porosity, and pre-treatment techniques such as steam explosion and pulse electric methods on agricultural biomass have demonstrated an improvement in pellet (compact) quality, that can be attributed to the changes in the lignocellulosic components and distribution (Ade-Omowaye et al., 2001; Bagby, 1982; Bhazal et al., 2003; Focher et al., 1998).

Structural characteristics and chemical compounds distribution of agricultural biomass at microscopic level before and after pre-treatment, and after densification can be studied using Infrared (IR) and Raman spectromicroscopy. This could reveal structural and chemical changes that occur when particular combinations of treatment variables (temperature, pressure, hold time, moisture content, etc.) are applied to produce an optimized and high quality pelletized/densified product development. To the knowledge of the authors, no such studies have been conducted to determine the structural characteristics and chemical components distribution in agricultural biomass using IR and Raman methods enabling it suitable for biorefineries. Therefore, the objectives of this study are:

- to review the structural and chemical characteristics of agriculture-based lignocellulosic biomass;
- to review the concepts and application of IR and Raman spectromicroscopy methods for biomass research; and
- to explore basic concepts, and evaluate the strengths and drawbacks of spectromicroscopy as applied to lignocellulosic material.

4.2.2 Lignocellulosic Material

Lignocellulosic material refers to plant biomass that is composed of cellulose, hemicellulose, and lignin (Lin and Tanaka 2006). The major combustible component of non-food energy crops is cellulose, followed by lignin. Non-food energy crops are more energy efficient than edible energy crops that have a large starch component (Holt-Gimenez 2007).

4.2.2.1 Cellulose

Cellulose is an organic polysaccharide (Figure 4.1) consisting of a linear chain of several hundred to over nine thousand β(1→4) linked D-glucose $(C_6H_{10}O_5)_n$ units (Crawford, 1981; Updegraff, 1969). Cellulose, a fibrous, tough, water-insoluble substance, is found in the cell walls of plants, particularly in the stalks, stems, trunks and all the woody portions of the plant body (Nelson and Cox 2005). Cellulose comprises 40-60% of the dry weight of plant material (the cellulose content of cotton is 90% and that of wood is 50%) (Encyclopædia Britannica, 2008; USDE, 2006). The multiple hydroxyl groups on the glucose residues from one chain form hydrogen bonds with oxygen molecules on another chain, holding the chains firmly together side-by-side and forming *microfibrils* with high tensile strength (Figure 4.2). This strength is important in cell walls, where they are meshed into a carbohydrate *matrix*, conferring rigidity to plant cells (Murphy and McCarthy, 2005).

Zandersons and co-workers (2004) and Shaw (2008) reported that binding of wood material during hot pressing / densification is mainly dependent on the transition of cellulose into the amorphous state. According to Hon (1989), due to the semi-crystalline structure, hydrogen bonded cellulose cannot be dissolved easily in conventional solvents, and it cannot be melted before it burns; hence, cellulose itself is not a suitable adhesive. This can be overcome by breaking the hydrogen bonds, thus making the cellulose molecule more flexible (Hon, 1989). Cellulose requires a temperature of 320°C and pressure of 25 MPa to become amorphous in water (Deguchi et al., 2006).

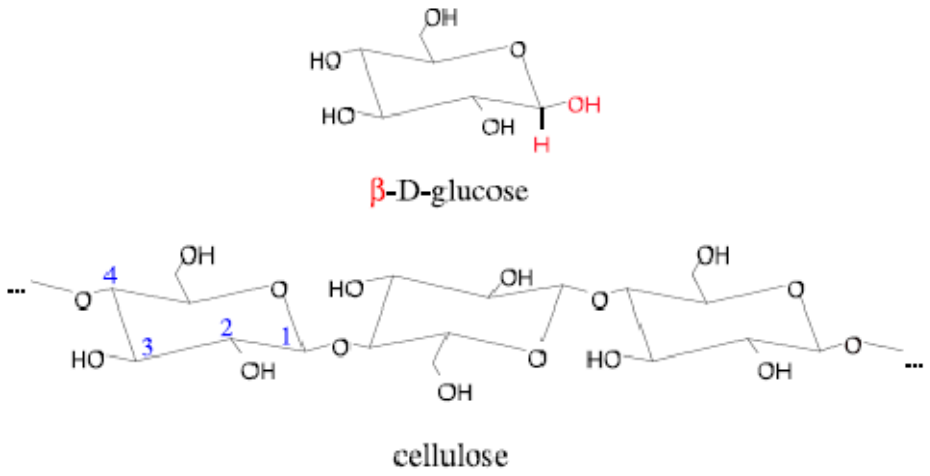


Figure 4.1: The glucose unit and the cellulose chain (Vainio, 2007).

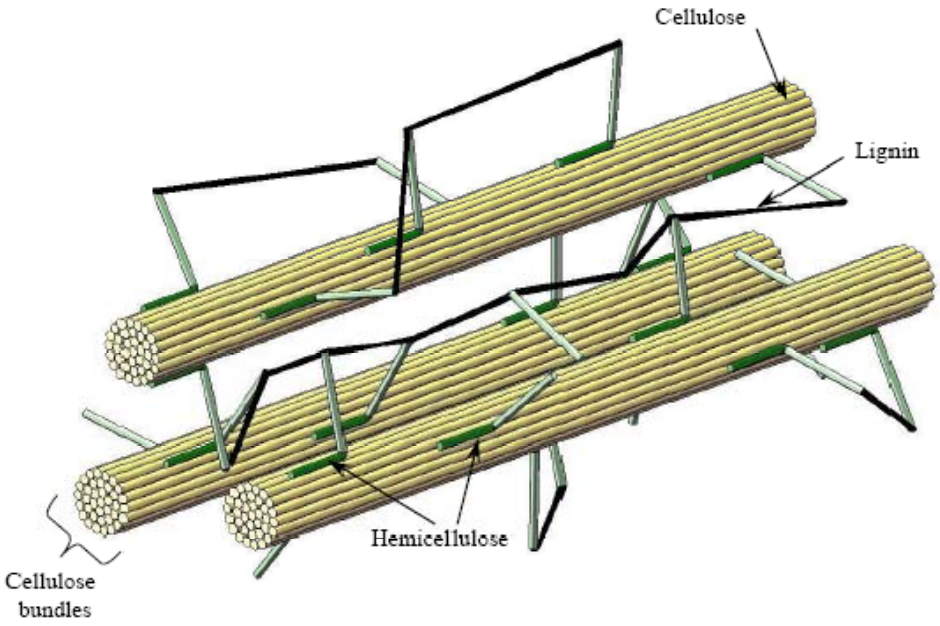


Figure 4.2: Location and arrangement of cellulose microfibrils in plant cell walls (Murphy and McCarthy, 2005; Shaw, 2008).

4.2.2.2 Hemicellulose

Hemicellulose is made of several heteropolymers (matrix polysaccharides) present in almost all plant cell walls along with cellulose (Figure 4.2). While cellulose is crystalline, strong, and resistant to hydrolysis; hemicellulose has a random, amorphous structure with less strength. Hemicellulose is a polysaccharide related to cellulose and comprises 20-40% of the biomass of most plants. In contrast to cellulose, hemicellulose is derived from several sugars in addition to glucose, including especially xylose but also mannose, galactose, rhamnose and arabinose (Shambe and Kennedy, 1985). Branching in hemicellulose produces an amorphous structure that is more easily hydrolyzed than cellulose (Shaw, 2008). Also, hemicellulose can be dissolved in strong alkali solutions. Hemicellulose provides structural integrity to the cell. Some researchers believe that natural bonding may occur due to the adhesive properties of degraded hemicellulose (Bhattacharya et al., 1989).

4.2.2.3 Lignin

Lignin is a complex chemical compound most commonly derived from wood and is an integral part of the cell walls of plants (Lebo et al., 2001; Zandersons et al., 2004). The compound has several unusual properties as a biopolymer, not the least its heterogeneity in lacking a defined primary structure. Lignin fills the spaces in the cell wall between cellulose and hemicellulose (Figure 4.2). It is covalently linked to hemicellulose and thereby crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and consequently to the whole plant structure (Chabannes et al., 2001). Different types of lignin have been described depending on the source and means of isolation (Lignin and its Properties, 2001).

There are three monomers of lignin, methoxylated to various degrees: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 4.3) (Freudenberg and Nash, 1968). These are incorporated into lignin in the form of the phenylpropanoids p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively (Boerjan et al., 2003). Gymnosperms have a lignin that consists almost entirely of G with small quantities of H. The dicotyledonic angiosperms is more often a mixture of G and S (with very little H), and monocotyledonic lignin is a mixture of all three (Boerjan et al., 2003). Many grasses have mostly G, while some plants have mainly S. All

lignin contain small amounts of incomplete or modified monolignols, and other monomers are prominent in non-woody plants (Ralph et al., 2001).

Lignin acts as a binder for the cellulose fibres (Figure 4.2). van Dam and co-workers (2004) have reported that lignin can be used as an intrinsic resin in binderless board production due to the fact that when lignin melts (temperatures above 140°C), it exhibits thermosetting properties. Lignin is the component that permits adhesion in the wood structure, and is a rigidifying and bulking agent (Anglès et al., 2001). Lehtikangas (2001) stated that water (8-15%) in pellets will reduce the softening temperature of lignin to 100-135°C by plasticizing the molecular chains. The adhesive properties of thermally softened lignin are thought to contribute considerably to the strength characteristics of briquettes made of lignocellulosic materials (Granada et al., 2002; Shaw, 2008).

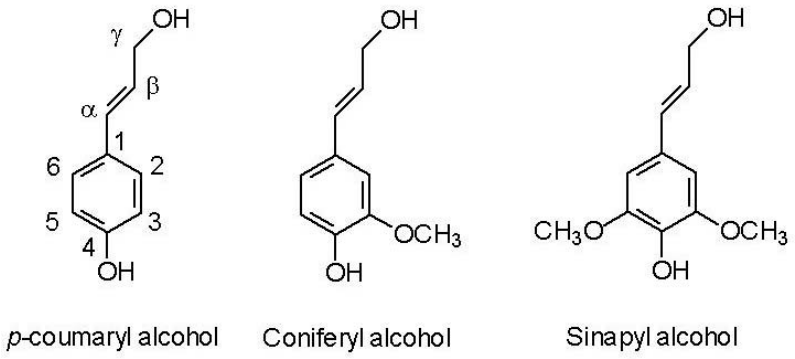


Figure 4.3: The three common monolignols (Freudenberg and Nash, 1968).

It is apparent that the application of various pre-processing and pre-treatment methods to enhance the availability and distribution of lignin is critical. Various traditional and proximate analysis methods are available to determine the chemical composition of lignocellulosic biomass. However, there is a lack of literature and understanding to determine chemical compounds distribution of agricultural biomass at microscopic level before and after pre-treatment, and after densification using IR and Raman spectromicroscopy. Therefore, the following sections will

explore the basic concepts of IR and Raman spectromicroscopy as applied to lignocellulosic biomass.

4.2.3 Vibrational and Rotational Spectroscopy

Spectroscopy may be defined as the study of the quantized interaction of electromagnetic radiations with matter. The electromagnetic radiations are produced by the oscillation of electric charge on an atom in a molecule (Yadav, 2005). Electromagnetic radiation is characterized by its wavelength λ (the length of one wave, cm), its frequency ν (the number of vibrations per unit time, s^{-1}), and its wavenumber $\bar{\nu}$ (the number of waves per unit length). The wavenumber expressed in cm^{-1} is the number of waves in a 1 cm-long wavetrain (Colthup et al., 1990). The wavenumber $\bar{\nu}$, in waves per centimetre (cm^{-1}), is related to the other parameters by (equation 1)

$$\bar{\nu} = \frac{\nu}{\left(c/n\right)} = \frac{1}{\lambda} \tag{1}$$

where:

c = velocity of light in vacuum (2.998×10^{10} cm/s), and

(c/n) = velocity of light in a medium whose refractive index is n, in which the wavenumber is measured.

It is important to understand the distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms (equation 2):

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} \tag{2}$$

In the above equation, the translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. The rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy

component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean centre of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring (Coates, 2000). Energy E in eV for a single photon is given by equation (3):

$$E = h\nu = \frac{hc}{\lambda} \tag{3}$$

where: h = Planck's constant (6.6256×10^{-34} J s**)**

4.2.3.1 Electromagnetic Radiation and Spectrum

Electromagnetic spectrum covers a very wide range of electromagnetic radiations. The arrangement of all types of electromagnetic radiations in order of their wavelengths or frequencies is shown in Figure 4.4.

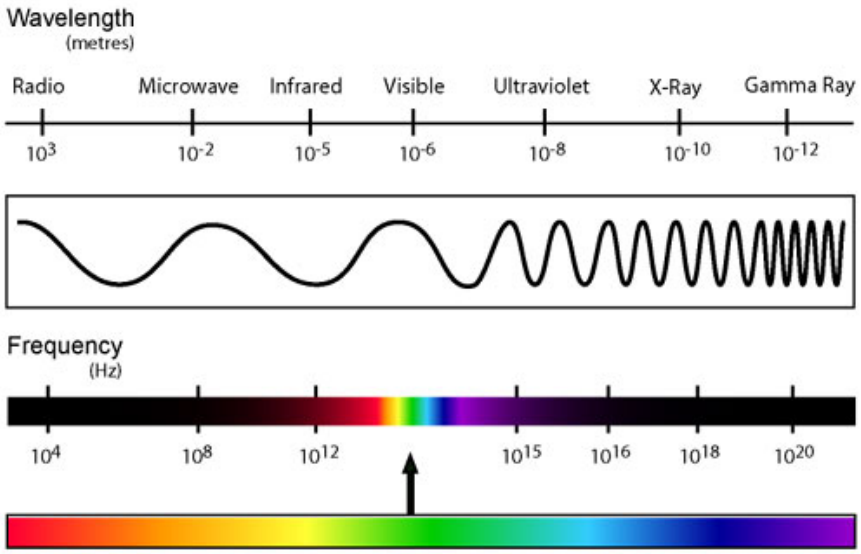


Figure 4.4: Electromagnetic spectrum (Colour Therapy Healing, 2008).

4.2.3.2 Absorption and Emission Spectra

When electromagnetic radiation is passed through an organic compound, it may be absorbed to induce electronic, vibrational and rotational transitions in the molecules. The energy required for each of these transitions is quantized. Thus, only the radiation supplying the required quantum (photon) of energy is absorbed and the remaining portion of the incident radiations is transmitted. Generally, a spectrometer records an absorption spectrum as a plot of the intensity of absorbed or transmitted radiations versus their wavelengths or frequencies and is called absorption spectra (Figure 4.5) (Schienmann, 1970; Williams and Fleming, 1966; Yadav, 2005).

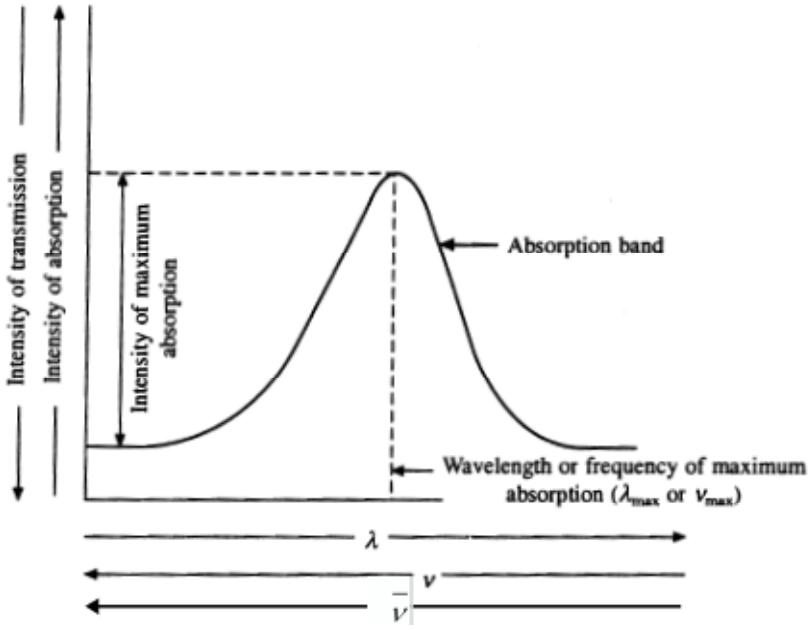


Figure 4.5: Schematic of absorption spectra (Yadav, 2005).

4.2.4 Infrared Spectromicroscopy

With the introduction of the IR spectromicroscopy, it is possible to measure spectra of objects as well as structures on the micrometer scale. Analysis of biological tissues became an important

area of interest due to the possibility to perform chemical analysis on a very small scale and link it to morphology (Budevska, 2002).

IR spectroscopy deals with the recording of the absorption of radiations in the infrared region of the electromagnetic spectrum. The position of a given infrared absorption is expressed in terms of wavenumber $\bar{\nu}$ (cm^{-1}) as it is directly proportional to energy. The ordinary infrared region 4000-667 cm^{-1} is of greatest practical use to organic chemists. The region 12,500-4000 cm^{-1} is called the near infrared and the region 667-50 cm^{-1} as the far infrared region. The absorption of infrared radiation by a molecule occurs due to quantized vibrational and rotational energy changes when it is subjected to infrared irradiation (Colthup et al., 1990; Yadav, 2005).

When a molecule absorbs IR radiation below 100 cm^{-1}, the absorbed radiation causes transitions in its rotational energy levels. Since these energy levels are quantized, a molecular rotational spectrum consists of discrete lines. When a molecule absorbs IR radiation in the range 100-10,000 cm^{-1}, the absorbed radiation causes transitions in its vibrational energy levels. These energy levels are also quantized, but vibrational spectra appear as bands rather than discrete lines. The rotational energy levels of a molecule are far less than that between its vibrational energy levels. Thus, a single transition in vibrational energy levels is accompanied by a large number of transitions in rotational energy levels and so the vibrational spectra appear as vibrational-rotational bands instead of discrete lines (Colthup et al., 1990; Yadav, 2005).

Infrared radiation is absorbed when the oscillating dipole moment, due to a molecular vibration, interacts with the oscillating electric field of the infrared beam. This interaction occurs and hence, an absorption band appears only when a molecular vibration produces a change in the dipole moment of the molecule. Otherwise, the vibration is said to be infrared inactive and will show no absorption band in the infrared spectrum. Usually, the larger the change in dipole moment, the higher is the intensity of absorption. It is not necessary for a molecule to have a permanent dipole moment for IR absorption (Yadav 2005).

4.2.4.1 Calculation of Vibrational Frequencies

The characteristic frequencies of particular combination of atoms within a molecule could be explained by the basic model of the simple harmonic oscillator and its modification to account for anharmonicity (Coates, 2000). Because of the importance in the study of molecular

vibrations, the classical vibrational frequency for a diatomic molecule will be derived using a model represented by two masses m_1 and m_2 connected by a mass-less spring (Colthup et al., 1990) (Figure 4.6).

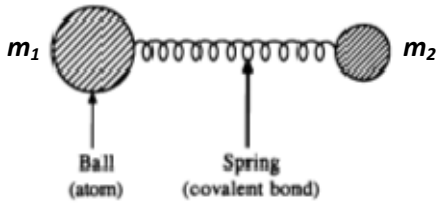


Figure 4.6: Representation of atoms using a simple harmonic oscillator model (Yadav, 2005).

Hooke's law could be used to express the fundamental vibrational frequency of a molecular ensemble (equation 4) (Coates, 2000).

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} \tag{4}$$

where:

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, m_1 and m_2 are the masses (g) of the atoms linked to the particular bond; and

f = force constant of the bond in dynes/cm.

This simple equation provides a link between the strength (or springiness) of the covalent bond between two atoms (or molecular fragments), the mass of the interacting atoms and the frequency of vibration. This simple model does not account for repulsion and attraction of the electron cloud at the extremes of the vibration, and does not accommodate the concept of bond dissociation at high levels of absorbed energy (Coates, 2000).

4.2.4.2 Fundamental Molecular Vibrations

The IR spectra of polyatomic molecules may exhibit more than one vibrational absorption band. The number of these bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degrees of freedom of the molecule. The degrees of freedom

of a molecule are equal to the total degrees of freedom of its individual atoms. Each atom has three degrees of freedom corresponding to the three Cartesian coordinates (x, y and z) necessary to describe its position relative to other atoms in the molecule. Therefore, a molecule having *n* atoms will have 3*n* degrees of freedom. In case of a non-linear molecule, three of the degrees of freedom describe rotation and three describe translation. Thus, the remaining $(3n - 3 - 3) = 3n - 6$ degrees of freedom are its vibrational degrees of freedom or fundamental vibrations (Coates, 2000; Colthup et al., 1990; Yadav, 2005).

In case of a linear molecule, only two degrees of freedom describe rotation (because rotation around its axis of linearity does not change the positions of the atom) and three describe translation. Thus, the remaining $(3n - 2 - 3) = 3n - 5$ degrees of freedom are vibrational degrees of freedom or fundamental vibrations (Coates, 2000; Colthup et al., 1990; Yadav, 2005).

The two types (modes) of fundamental molecular vibrations known are: a) stretching; and b) bending vibrations (deformations) (Coates, 2008; Colthup et al., 1990; Yadav, 2005).

4.2.4.2.1 Stretching Vibrations

In stretching vibrations, the distance between two atoms increases or decreases, but the atoms remain in the same bond axis. Stretching vibrations are of two types (Colthup et al., 1990; Yadav 2005):

a) Symmetrical stretching - in this mode of vibration, the movement of atoms with respect to the common (or central) atom is simultaneously in the same direction along the same bond axis (Figure 4.7(a)); and
b) Asymmetrical stretching - in this vibration, one atom approaches the common atom while the other departs from it (Figure 4.7(b)).

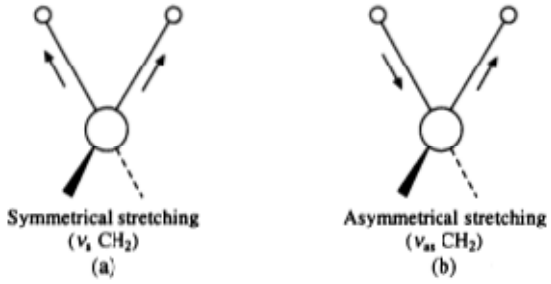


Figure 4.7: Stretching vibrations of CH_2 group ($\nu\, CH_2$) (Yadav, 2005).

In practice, various other deformation motions (angular changes), such as bending and twisting about certain centers within a molecule, also have impact, and contribute to the overall absorption spectrum. By rationalizing the effort needed to move the atoms relative to each other, one can appreciate that it takes less energy to bend a bond than to stretch it. Consequently, the stretching absorptions of a vibrating chemical bond occur at higher frequencies (wavenumbers) than the corresponding bending or bond deformation vibrations, with the understanding that energy and frequency are proportionally related. In addition, it takes slightly more energy to excite a molecule to an asymmetric than a symmetric vibration (Coates, 2000).

4.2.4.2.2 Bending Vibrations (Deformations)

In bending vibrations, the positions of the atoms change with respect to their original bond axes. Bending vibrations are of four types (Colthup et al., 1990; Yadav, 2005):

a) Scissoring - in this mode of vibration, the movement of atoms is in the opposite direction with change in their bond axes as well as in the bond angle they form with the central atom (Figure 4.8(a));
b) Rocking - in this vibration, the movement of atoms takes place in the same direction with change in their bond axes (Figure 4.8(b)). Both scissoring and rocking are in-plane bendings;
c) Wagging - in this vibration, two atoms simultaneously move above and below the plane with respect to the common atom (Figure 4.8(c)); and
d) Twisting - in this mode of vibration, one of the atom moves up and the other moves down the plane with respect to the common atom (Figure 4.8(d)).

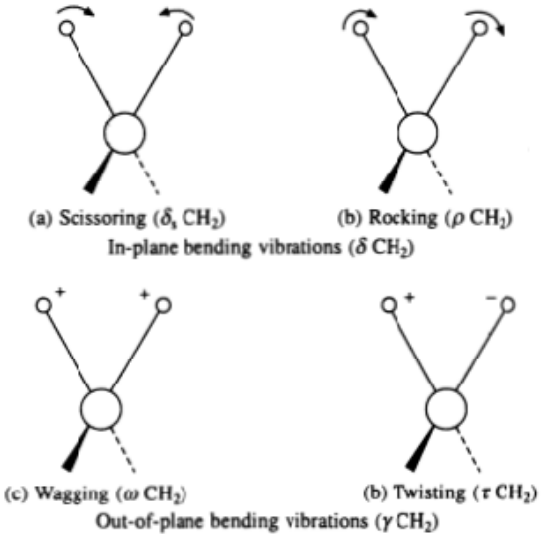


Figure 4.8: Bending vibrations (deformations) of CH_2 group (+ and – signs indicate movements perpendicular to the plane of the paper) (Yadav, 2005).

4.2.4.3 Fingerprint Region

It is not possible for any two different compounds to have exactly the same IR spectrum. Therefore, the IR spectrum of a compound is called its fingerprint. The region below 1500 cm^{-1} is called fingerprint region because every compound has unique absorption pattern in this region. The fingerprint region contains many absorption bands caused by bending vibrations as well as absorption bands caused by stretching vibrations. Since the number of bending vibrations in a molecule is much greater than its stretching vibrations, the fingerprint region is rich in absorption bands and shoulders. Thus, the superimposability of IR bands of the spectra of any two different compounds becomes impossible in this region. However, similar compounds may show very similar spectra above 1500 cm^{-1} (Coates, 2000).

4.2.5 Raman Spectromicroscopy

Infrared and Raman spectroscopy are closely related as both originate from the transition in vibrational and rotational energy levels of the molecule on absorption of radiations. The intensity of IR absorption depends on the change in dipole moment of the bond, whereas Raman intensity depends on the change in polarizability of the bond accompanying the excitation. Thus, an electrically symmetrical bond (i.e. having no dipole moment) does not absorb in IR region

(i.e. the transition is forbidden) but it does absorb in Raman scattering (i.e. the transition is allowed). In other words, an electrically symmetrical bond is Raman active but IR inactive. However, an electrically unsymmetrical bond may be IR active and Raman inactive or both IR and Raman active (Anderson, 1973; Colthup et al., 1990).

IR and Raman spectroscopy are complementary techniques. For example, studies on bond angles, bond lengths and other structural confirmations require Raman data in addition to IR analysis (Yadav, 2005).

According to Raman effect, when a beam of strong radiation of a definite frequency is passed through a transparent substance (gas, liquid or solid), the radiation scattered at right angles has not only the original frequency but also some other frequencies which are generally lower and occasionally higher than that of the incident radiation. This is known as Raman scattering or *Raman effect*. The spectral lines resulting from lower frequencies than that of the incident radiation are called *Stokes lines* and those from higher frequencies are called *anti-Stokes lines*. The spectral lines whose frequencies have been modified in *Raman effect* are called Raman lines. Thus, Stokes and anti-Stokes lines are *Raman lines*. The Raman spectra are a manifestation of *Raman effect* which is accompanied by transitions in vibrational and rotational energy levels of the molecule. Similar to IR spectra, the position of spectral lines (or bands) in Raman spectra are also reported in wavenumbers (cm^{-1}) (Anderson, 1973; Colthup et al., 1964).

The incident light is associated with energy $h\nu_i$, a part of which is used for causing transitions from lower to higher vibrational and rotational energy levels, so the scattered radiation has a lower energy content $h\nu_s$ and thus a new line (Raman line) appears in the spectrum. Raman also discovered that the frequency difference $\Delta\nu$ between the incident frequency ν_i and any scattered frequency ν_s is constant and characteristic of the substance exposed to radiation and is completely independent from the frequency of the incident radiation ν_i. $\Delta\nu$ is known as *Raman frequency shift* or *Raman shift* and is given by the Equation (5) (Anderson, 1973; Yadav, 2005).

$$\Delta\nu = \nu_i - \nu_s \tag{5}$$

where $\Delta\nu$ is positive for Stokes line and negative for anti-Stokes lines. Although Raman shifts $\Delta\nu$ correspond to IR absorption or emission, IR and Raman spectra of a substance are not always identical.

4.2.6 Applications of Vibrational Spectromicroscopy for Agricultural Biomass

The ability to produce qualitative and quantitative analytical data for samples with minimum or no sample preparation has made the vibrational spectroscopic approach the preferred one in many cases where speed and high throughput are of great importance. The ability to fingerprint the chemical composition in a spatially-resolved manner will, most likely, prove to be unique and most valuable, especially in the characterization of agricultural materials. Applications developed for agricultural purposes span a wide range including satellite and aerial remote sensing, macroscopic imaging for quality control and in vivo measurements, and microscopic applications aimed at increasing the fundamental understanding of plant physiology on the cellular level (Budevska, 2002).

IR and Raman spectroscopy are complementary techniques that provide information on molecular structure. By combining spectroscopy with microscopy, molecular information can be obtained with great spatial resolution (at the micrometer scale) at the microscopic level (Thygesen *et al.* 2003).

4.2.6.1 Applications of IR Spectromicroscopy

Among all the properties of an organic compound, no single property gives as much information about the compound's structure as its IR spectrum. Thus, IR spectroscopy is the most widely used method for the compositional determination of organic compounds. The basic reason why IR spectra are of such value to organic chemists is that molecular vibrations depend on interatomic distances, bond angles and bond strengths, rather than on bulk properties of the compound. Thus, these vibrational frequencies provide a molecular fingerprint which enables the identification of the compound either in the pure state or in mixtures (Yadav, 2005).

Synchrotron based IR spectromicroscopy has better signal to noise ratio and spatial resolution compared to globar sources. The technique is used to identify molecular constituents in biological samples from their vibrational spectra in the mid-IR region (4000-667 cm^{-1}), and is

capable of exploring the molecular chemistry (structural make-up) within microstructures of biological tissues at a cellular level without destruction of internal structures at a high spatial resolution (3-10 μ m) (Marinkovic et al., 2002; Yu et al., 2007).

A drawback of globar-source IR spectromicroscopy is the diffraction effects which result in reduced aperture size that limit the field of view to a small region of interest. At the same time, less light overall results in a decrease in the signal-to-noise ratio. For this kind of study on a plant tissue's molecular structural-chemical features for which spectral data need to be collected at the diffraction limit (a few micrometers) in each spatial dimension, only advanced synchrotron and free-electron lasers can be used. Furthermore, the brightness of conventional bench-top IR source is lower by two to three orders of magnitude (Raab and Martin, 2001).

The IR spectromicroscopy have been used to study chemical composition and distribution of various lignocellulosic biomasses as applied to food, feed, biocomposite, textile, and paper and pulp industries. The summary of IR study on various lignocellulosic materials is listed in Table 4.1. Yu et al. (2007) characterized the molecular chemistry of the internal structure of wheat and reported both its structural chemical make-up and nutrient component matrix by analyzing the intensity and spatial distribution of molecular functional groups within the intact seed using advanced synchrotron-based IR spectromicroscopy. A spectral examination of wheat tissue by Yu et al. (2007) provided a unique absorption band of lignin at 1510 cm^{-1} in the mid-IR region of the electromagnetic spectrum. This is considered to be indicative of the aromatic character of the lignin. An aromatic compound gives two major bands at 1600 and 1510 cm^{-1}, resulting from quadrant and semicircle ring stretching, respectively (Colthup et al., 1990). Yu et al. (2007) observed strong bands for both structural and non-structural carbohydrates, particularly in the 1100-1025 cm^{-1} region. A presence of moderate intensity bands at 1420, 1370 and 1335 cm^{-1} are characteristics of structural carbohydrates. A peak at 1246 cm^{-1} is used to indicate the presence of structural carbohydrate such as cellulose (Wetzel et al., 1998; Wetzel, 2001).

Himmelsbach et al. (1998) performed experiments to determine the distribution of chemical components in two varieties of flax stems. They have observed bands at 1595 and 1510 cm^{-1} located in the core, cuticle and epidermal tissue and assigned it to aromatic compounds (lignin). Cellulose was monitored by the band at 1335 cm^{-1} and acetylated hemicellulosic materials were monitored at 1250 cm^{-1}.

Stewart et al. (1995) used IR and Raman spectroscopy techniques to investigate the changes in the composition and structure of oak wood and barley straw that had been subjected to chemical and biochemical treatments. Both spectral techniques have been shown to be useful in the analysis of plant and cell walls. The use of both techniques in isolation provided general structural and compositional information of oak wood and barley after biochemical treatments (Table 4.1).

Wilson et al. (2000) performed IR spectromicroscopy analysis of the onion cell and determined the orientation of macromolecules in single cell wall. The IR spectrum of onion was dominated by absorption bands of cellulose and pectin, while minor constituents such as protein, ferulic acid, lignin and hemicelluloses were also detected (Table 4.1).

Yu (2005) used synchrotron-based IR spectromicroscopy to determine molecular chemistry of various feeds (including grain corn and oat hull tissues) to reveal their ultra-structural and chemical composition (Table 4.1). The molecular chemical information can be linked to structural and nutritional information. Such information can also be used for biological structural study.

Table 4.1: Summary of FT-IR spectra obtained for various lignocellulosic materials.

Material	Wavenumber (cm^{-1})	Researcher(s)
Lignin		
Wheat Seed Tissue	1600 – quadrant ring stretching – aromatic lignin	Colthup et al., 1990; Yu et al., 2007
	1510 – semicircle ring stretching – aromatic lignin	
Wheat Straw	1595 – very strong aromatic ring stretch; aromatic C-O stretching	Revol, 1982; Stewart et al., 1995
	1510 – very strong aromatic ring stretch; aromatic C-O stretching	
Steam Exploded Wheat Straw	1513 & 1433 – aromatic C=C stretch	Sun et al., 2005
	1473 & 1380 – C-H symmetric and	

	asymmetric deformation	
	1327 – C-C and C-O skeletal stretch	
Flax Stems	1595 – phenylpropanoid polymer	Himmelsbach et al., 1998
	1510 – phenylpropanoid polymer	
Corn Kernel	1514 semicircle stretching – para-substituted benzene rings	Lin-Vein et al., 1991; Budevska, 2002
Barley Straw	1595 – aromatic skeletal vibrations plus C=O stretch	Lin and Dence, 1992; Stewart et al., 1995
	1510 –aromatic ring stretch	
Grain Corn Tissue	1510 – aromatic lignin characteristics	Yu, 2005
Oat Hull Tissue	1510 – aromatic lignin characteristics	Yu, 2005
Cellulose		
Wheat Seed Tissue	1420 Weak C-O stretching	Yu et al., 2007; Wetzel et al., 1998
	1370 Weak C-O stretching	
	1335 Weak C-O stretching	
	1246 Strong C-O stretching	
Wheat Straw	1162, 1130, 1098	Michell, 1990; Stewart et al., 1995; Yu et al., 2007
	900 – anti-symmetric out-of-plane ring stretch of amorphous cellulose; C-O stretching	
	1500-1300 – C-H bending	
Flax Stems	1335	Himmelsbach et al., 1998
Barley Straw	1130 – ? (reason not reported)	Stewart et al., 1995
	1098 – weak absorbance	
	900 – anti-symmetric out-of-plane ring stretch of amorphous cellulose; C-O	

	stretching	
Onion	1430 – CH_2 in-plane bending vibrations 1336 – C-H ring in-plane bending vibrations 1162 – C-O-C ring vibrational stretching 1125/1110 – C-O and C-C ring vibrational stretching 1060 – C-O stretching and O-C-H in-plane bending vibrations 1035 – C-O, C=C and C-C-O vibrational stretching 985 – OCH_3	Schulz and Baranska, 2007; Wilson et al., 2000
Grain Corn Tissue	1246 – cellulosic compounds	Yu, 2005
Oat Hull Tissue	1246 – cellulosic compounds	Yu, 2005
Hemicellulose		
Wheat Straw	1735 – ? (reason not reported)	Chen et al., 1997; Gastaldi et al., 1998
Flax Stems	1250 – Acetylated Hemicellulose	Himmelsbach et al., 1998
Onion	815 – ? (reason not reported)	Schulz and Baranska, 2007; Wilson et al., 2000

Note: The references of Researchers provided in Table 4.1 – Column 3 are for both assignment and observed wavenumbers

4.2.6.2 Applications of Raman Spectromicroscopy

Although cellulose and lignocellulosic materials have been studied using conventional Raman spectroscopy, availability of the Raman instrumentation has made studying these materials more convenient (Agarwal, 1999). Many Raman studies of such materials have been published including studies of quantitative nature (Agarwal et al., 2003; Ona et al., 1998; Sun et al., 1997).

For *in situ* structural analysis of lignocellulosic materials, which are heterogeneous composites of cellulose, lignin and hemicellulose and whose microstructures are composed of morphologically distinct regions, Raman spectroscopy is a good technique. Capability to analyze microscopic regions is another important tool which makes Raman microscopy suitable (Turrell and Corsett, 1996). Further considering that presence of water in a sample is not a problem (unlike IR) and information on the orientation of macromolecular components can be obtained. Raman spectroscopy has capabilities that are not provided by any other method (Agarwal, 2008).

The use of Raman spectromicroscopy mapping has been explored for studies of flax stem (Himmelsbach et al., 1999). The results were in agreement with the one obtained with IR microscopic mapping (Himmelsbach et al., 1998).

Assignment of bands/wavenumbers in the Raman spectra of lignocellulosics is an important topic of research. Although some information is already available (Agarwal et al., 1997; Takei et al., 1995), research in this area needs to be accelerated considering that more and more lignin-containing materials are being studied using Raman spectroscopy, which is primarily responsible for the laser induced fluorescence. For interpreting the Raman spectrum of a multi-component material like lignocellulose, not only the contribution of each component needs to be identified but the latter needs to be assigned to component-specific structural units and/or functional groups (Agarwal, 2008).

In this context, note that Raman features of cellulose have already been assigned (Wiley and Atalla, 1987). Moreover, hemicellulose spectral assignments are expected to be very similar to that of cellulose (Agarwal and Ralph, 1997). Therefore, it is primarily lignin for which bands need to be assigned. Assignment for softwood-cellulose Raman bands is given in Table 4.2 (Agarwal, 1997).

Table 4.2: Assignment of bands in the FT-Raman spectrum of softwood-cellulose (Agarwal, 1997).

Wavenumber (cm^{-1})	Assignment[a]
330 sh[b]	Heavy atom bending
351 w	Some heavy atom stretching

380 m	Some heavy atom stretching
406 vw	not reported
435 m	Some heavy atom stretching
458 m	Some heavy atom stretching
492 w	not reported
520 m	Some heavy atom stretching
899 m	HCC and HCO bending at C6[c]
971 vw	Heavy atom (CC and CO) stretching
1000 vw	Heavy atom (CC and CO) stretching
1037 sh	Heavy atom (CC and CO) stretching
1063 sh	Heavy atom (CC and CO) stretching
1073 sh	Heavy atom (CC and CO) stretching
1095 s	Heavy atom (CC and CO) stretching
1123 s	Heavy atom (CC and CO) stretching
1149 sh	Heavy atom (CC and CO) stretching plus HCC and HCO bending
1298 sh	HCC and HCO bending
1338 m	HCC and HCO bending
1377 m	HCC, HCO and HOC bending
1456 m	HCH and HOC bending
2740 vw	not reported
2848 sh	CH and CH_2 stretching[d]
2895 vs	CH and CH_2 stretching

[a]Assignment based on reference (Wiley and Atalla, 1987)
[b]Note: vs is very strong; s is strong; m is medium; w is weak; vw is very weak; sh is shoulder. Band intensities are relative to other peaks in the spectrum.
[c]In reference (Wiley and Atalla, 1987) the band is at 913 cm^{-1}
[d]In reference (Wiley and Atalla, 1987) the band is at 2868 cm^{-1}

Further considering that lignin and hemicellulose molecular structures are somewhat different in different lignocellulosic materials (e.g., in softwood, hardwood and grasses), it is even more important that the goal of band assignment for each class of differing lignocellulosics be accomplished (Agarwal, 2008). When assignments of bands are available, one can evaluate how structural differences and similarities of lignin and carbohydrate polymers are reflected in their individual Raman spectra. For black spruce (softwood) lignin, Raman bands have been assigned (Table 4.3) (Agarwal et al., 1997).

Table 4.3: Assignment of bands in the FT-Raman spectrum of softwood lignin (Agarwal, 2008)

Wavenumber (cm^{-1})	Assignment[a]
357 w[b]	Skeletal deformation of aromatic rings, substituent groups and side chains
384 w	Skeletal deformation of aromatic rings, substituent groups and side chains
463 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
491 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
537 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
555 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
591 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
634 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
731 w	Skeletal deformation of aromatic rings, substituent groups and side chains
787 w	Skeletal deformation of aromatic rings, substituent groups and side chains
900 vw	Skeletal deformation of aromatic rings, substituent groups and side chains
926 vw	CCH wag
969 vw	CCH and -HC=CH- deformation
1033 w	C-O of aryl-O-CH_3 and aryl-OH
1102 w	Out of phase C-C-O stretch of phenol
1134 m	A mode of coniferaldehyde
1191 w	A phenol mode
1216 vw	aryl-O of aryl-OH and aryl-O-CH_3; guaiacyl ring (with C=O group) mode
1271 m	aryl-O of aryl-OH and aryl-O-CH_3; guaiacyl ring (with C=O group) mode
1297 sh	aryl-O of aryl-OH and aryl-O-CH_3; C=C stretch of coniferyl alcohol
1333 m	Aliphatic O-H bend
1363 sh	C-H bend in R_3C-H
1393 sh	Phenolic O-H bend
1428 w	O-CH_3 deformation; CH_2 scissoring; guaiacyl ring vibration

1454 m	O-CH_3 deformation; CH_2 scissoring; guaiacyl ring vibration
1508 vw	Aryl ring stretching, asymmetric
1602 vs	Aryl ring stretching, symmetric
1620 h	Ring conjugated C=C stretch of coniferaldehyde
1658 s	Ring conjugated C=C stretch of coniferyl alcohol; C=O stretch of coniferaldehyde
2843 m	C-H stretch in OCH_3, symmetric
2886 sh	C-H stretch in R_3C-H
2938 m	C-H stretch in OCH_3, asymmetric
3007 sh	C-H stretch in OCH_3, asymmetric
3065 m	Aromatic C-H stretch

[a]Assignment taken from reference Agarwal et al., 1997
[b]Note: vs is very strong; s is strong; m is medium; w is weak; vw is very weak; sh is shoulder. Band intensities are relative to other peaks in the spectrum.

Samples of flax (*Linum usitatissimum L.*) stem and its anatomical parts were studied by near-infrared Raman (NIR-Raman) spectroscopy to determine if the major chemical components of each could be detected by this method (Himmelsbach and Akin, 1998). The bands for cellulose were primarily observed in the fibres and hemicellulose polysaccharides were observed to be prevalent in bast tissue and fibres (Table 4.4).

Table 4.4: Regions assigned to cellulose and hemicellulose present in flax fibres (Himmelsbach and Akin, 1998; Jahn et al., 2002).

Wavenumber (cm^{-1})	Assignment
Cellulose	
3000-2800	C-H stretch region; OH/CH deformation; CH/CH_2 wag region
1500-1200	C-O stretch
1200-950	Ring mode region
1120 and 1098	Symmetrical C-O-C and asymmetrical C-O-C vibrational stretching
950-700	Side-group deformation region for COH, CCH and OCH
910-890	HCC and HCO bending at the C6
Hemicellulose	
890	HCC and HCO bending at C6
515-470	HCC and HCO bending at C6
2895	Very strong C-H stretch

4.2.7 Advantages and Disadvantages of IR and Raman Spectromicroscopy

Although Raman shifts fall in the IR region of the electromagnetic spectrum, Raman spectra are quite different from IR spectra (Colthup et al., 1990; Himmelsbach and Akin, 1998; Pistorius,

1995; Schenzel and Fischer, 2001; Schulz and Baranska, 2007; Thygesen et al., 2003; West, 1996; Williams and Manson, 1990; Yadav, 2005). Table 4.5 summarizes the advantages and disadvantages of IR and Raman spectra deduced from literature review performed in previous sections. Both techniques have been proved beneficial in obtaining chemical compound information and their spatial distribution in lignocellusic biomass, when applied in coordination.

Table 4.5: Advantages and disadvantages of IR and Raman spectroscopy

Infrared Spectra	Raman Spectra
These originate from absorption of radiation by vibrating and rotating molecules	These originate from scattering of radiation by vibrating and rotating molecules
IR spectroscopy detects vibrations during which the electrical dipole moment changes	Raman spectroscopy is based on the detection of vibrations during which the electrical polarisability changes
For liquid samples, generally, dilute solutions are preferred	Raman lines are weak in intensity, hence concentrated solutions are preferred to get enough intensity
Wet samples can not be used for spectroscopic study because the O-H stretching vibration is very strong in IR and will give false spectra	Wet or dry sample can be used for spectroscopic study because the O-H stretching vibration is very weak in Raman since O-H bonds are weakly polarized
Optical systems of IR spectrometer are made of NaCl, NaBr, KCl, KBr, etc.	Optical systems of Raman spectrometer are made of glass or quartz
Fluorescent/Photochemical reactions do not take place	Sometimes fluorescent/photochemical reactions take place in the frequency regions of Raman lines and so create difficulties
IR has high signal-to-noise ratio resulting in shorter sampling times	Signal-to-noise ratio is much lower, and if the sample fluoresces, measurements may even be impossible. Therefore, long sampling times and/or repeated samplings are desired
The IR spectromicroscopy has spatial resolution of $\geq 10\ \mu m^2$ (Thygesen *et al.* 2003) and does	Raman spectromicroscopy has the potential of a better spatial resolution ($\geq 1\ \mu m^2$) due to

not offer confocality i.e. it is not possible to focus on different planes below the sample surface	lower wavelengths used and is possible to focus on different planes below the sample surface
Method is accurate as well as very sensitive	Method is accurate but not very sensitive
These are recorded by using a beam of radiation having a large number of frequencies in the IR region	These are recorded by using a beam of monochromatic radiation
Homonuclear diatomic molecules are IR inactive	Homonuclear diatomic molecules are Raman active
IR spectroscopy has negligible concerns of heating the sample	Raman spectroscopy has the problem of heating the sample due to heat generated by the laser. Therefore, short sampling times are recommended to avoid any alteration to the sample
Studies by the IR spectra do not require a high degree of purity	Pure substances are required for studies by Raman spectra

4.3 Quantitative Analysis of Lignocellulosic Components of Non-Treated and Steam Exploded Barley, Canola, Oat and Wheat Straw using Fourier Transform Infrared Spectroscopy

4.3.1 Introduction

Agricultural (lignocellulosic) biomass residues such as barley, canola, oat and wheat straw have the potential to be used as the feedstock for the biofuel industry (Liu et al., 2005). After harvest, the low bulk density agricultural straw should be processed and densified for efficient handling and transportation, and reap the potential economic benefits.

It has been reported by Sokhansanj et al. (2005) that densified straw often results in poorly formed pellets or compacts, and are difficult to handle and costly to manufacture. This is

primarily due to the lack of complete understanding on the binding characteristics of biomass at the molecular level. The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). However, the effect of various pre-processing and pre-treatment methods on the lignocellulosic matrix at the molecular level is not well understood. Applications of pre-processing methods such as size reduction or increasing porosity, and pre-treatment techniques such as steam explosion and pulse electric field on agricultural biomass have demonstrated an improvement in pellet (compact) quality that can be attributed to the changes in the lignocellulosic components and distribution (Ade-Omowaye et al., 2001; Bagby, 1982; Bazhal et al., 2003; Focher et al., 1998). Therefore, it is critical to rapidly quantify the change in cellulose, hemicelluloses and lignin components of biomass due to application of pre-treatment methods.

Infrared spectroscopy has the potential to produce qualitative and quantitative analytical data for samples with minimum or no sample preparation, and at high speed and throughput (Budevska, 2002; Luypaert et al., 2003; Smola and Urleb, 2000; Tucker et al., 2000). Traditionally, chemical analyses of the individual components (e.g., lignin) of lignocellulosics have been performed by acid hydrolysis followed by gravimetric determination of lignin (Kelley et al., 2004). These methods can provide highly precise data. However, these methods are laborious, time-consuming, and, consequently, expensive to perform and sample throughput is limited. Hence, there is a need to develop analytical tools that can be used to rapidly and inexpensively measure the chemical composition of biomass (Kelley et al., 2004; Gelbrich et al., 2009; Vazquez et al., 2002).

One of the early studies on quantitative analysis of component mixtures of acetylsalicylic acid, salicylic acid and filler or binder with varying concentration using Fourier transform infrared (FTIR) photoacoustic spectroscopy (PAS) was performed by Rosenthal et al. (1998). They were able to develop partial least square models with high correlation coefficients. A study by Belton et al. (1987) successfully used FTIR spectroscopy for the quantitative analysis of protein and starch mixtures. Similarly, Moh et al. (1999) used FTIR spectroscopy to investigate and develop a foundation for the rapid determination of β-carotene content of crude palm oil. They have also developed separate partial least squares calibration models to predict β-carotene based on

spectral region from 976 to 926 cm^{-1} for FTIR spectroscopy. The use of infrared spectroscopy in the study of fats and oils has been reviewed by Guillen and Cabo (1997). Van de Voort et al. (1994) developed FTIR spectroscopy that operates in the mid infrared region (4000-400 cm^{-1}) and has been proven to be a powerful tool for quantitative analysis of fats and oils.

Rodrigues et al. (1998) have obtained linear correlation with high regression coefficients to estimate lignin content in *Eucalyptus globulus* wood, using bands characteristic for lignin in FTIR spectra and bands characteristic for carbohydrate as reference. Similarly, the estimate of lignin and polysaccharide content in eucalyptus and pine acetosolv pulps was performed by Vazquez et al. (2002) using FTIR spectroscopy to obtain mathematical models. They have employed a STEPWISE regression analysis for the selection of spectra bands that correlate satisfactorily with experimental results.

The characterization and stages of organic municipal solid waste matter decomposition during mechanical and biological treatment was determined using the FTIR spectroscopy (Smidt and Schwanninger, 2005). The technique was used to observe the maturity and stability of waste organic matter based on the missing spectral bands that indicate metabolic activities.

Tucker et al. (2000) successfully performed the analysis of glucose, mannose, xylose, and acetic acid using FTIR spectroscopy in conjunction with high-performance liquid chromatography for the quantitative analysis of liquors from dilute-acid-pretreated softwood and hardwood slurries. Similarly, Bjarnestad and Dahlman (2002) employed the FTIR PAS technique in combination with partial least square analysis to accurately predict the contents of carbohydrates in hardwood and softwood pulps. In addition, the analytical procedure developed could be used on a routine basis to quantify pulp constituents with considerably less effort and in shorter time than is possible using chemical analysis. Also, Nuopponen et al. (2005) successfully studied the chemical modification of Scots pine wood in thermal treatments in the range of 100-240^{o}C using the FTIR technique with the assistance of PAS detector. They have established that lignin became partly extractable by acetone at 180^{o}C and the amount of soluble lignin increased with an increase in temperature up to 220^{o}C. In addition, degradation of hemicelluloses was also detected from the FTIR spectral data.

Gelbrich et al. (2009) characterized the bacterial degradation of waterlogged softwood samples using FTIR spectroscopy. They have established a linear relationship between lignin content and the extent of bacterial degradation in softwood.

The literature review of lignocellulosic biomass have indicated that infrared spectroscopy could be used successfully to study the chemical structure of cellulose, hemicellulose and lignin in various agricultural biomasses as applied to food, feed, biocomposite, textile, and paper and pulp industries. It is evident from previous studies that FTIR spectroscopy has the potential to perform qualitative and quantitative analysis of agricultural (lignocellulosic) biomass to determine change in cellulose-hemicellulose-lignin composition prior to and after application of various pre-processing and pre-treatment methods. Therefore, the objective of this work was to estimate critical parameters in analytical specification of lignocellulosic biomass and consequently, to develop and validate a rapid method for the qualitative and quantitative analysis of cellulose-hemicellulose-lignin composition of non-treated and steam exploded barley, canola, oat and wheat straw using FTIR PAS.

4.3.2 Materials and Method

4.3.2.1 Sample Material Preparation

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for FTIR spectroscopy experiments. The straw samples were acquired in square bale form during the summer of 2008 from the Central Butte area of Saskatchewan, Canada. The moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (w.b.), respectively. The moisture content was determined using ASABE Standard S358.2 (ASABE, 2006a).

The non-treated straw samples were manually chopped using a pair of scissors and subsequently fine-ground in a precision grinder (Falling Number, Model No. 111739, Huddinge, Sweden) having a screen size of 1.0 mm. The steam explosion of straw was performed at the FPInnovations, Forintek pilot plant continuous steam explosion facility at Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized disc refiner having a plate gap of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive set to operate at 2000 rpm was used to steam explode the straw. Similar to non-treated straw, the steam exploded straw was ground in a precision grinder having a screen size of 1.0 mm.

4.3.2.2 Reference Material Preparation

Quantitative analysis of cellulose, hemicelluloses and lignin composition of non-treated and steam exploded sample material is critical in order to predict and evaluate the change in natural binding characteristics of straw. Therefore, pure cellulose (microcrystalline powder), hemicelluloses (xylan from birch wood) and lignin (hydrolytic) powders were obtained from Sigma-Aldrich Canada Ltd. (St. Louis, MO), and were subsequently mixed in different proportions (Table 4.6) to determine the relationship (predictive models) between their respective quantity in the mixture and representative FTIR spectra. Carbon black powder reference spectrum was used to correct for FTIR wavenumber-dependent instrumental effects.

Table 4.6: Pure cellulose, hemicelluloses and lignin mixtures used to obtain reference spectra.

Reference Mixtures	Lignin (%)	Cellulose (%)	Hemicellulose (%)
C1H0L0*	100	0	0
C0H1L0	0	100	0
C0H0L1	0	0	100
C5H2L2	50	25	25
C2H5L2	25	50	25
C2H2L5	25	25	50
C7H2L0	75	25	0
C2H7L0	25	75	0
C2H0L7	25	0	75
C0H2L7	0	25	75
C3H3L3	33	33	33
C7H0L2	75	0	25
C0H7L2	0	75	25

*Note: C, H and L represents Cellulose, Hemicellulose and Lignin, respectively

4.3.2.3 Lignocellulosic Composition of Agricultural Biomass

It is essential to validate the predicted lignocellulosic quantity of sample agricultural straw (section 4.3.2.1) using correlation models developed from the analysis of reference material spectra (section 4.3.2.2). The experimental ligniocellulosic composition of agricultural straw was performed in replicates of three at the Agriculture and Agri-Food Canada, Saskatoon lab facility using the modified NREL LAP method for "Determination of Structural Carbohydrates

and Lignin in Biomass" (Sluiter et al., 2008). This procedure uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. During this process, the lignin fractionates into acid insoluble material and acid soluble material, while the polymeric carbohydrates are hydrolyzed into the monomeric forms, which are soluble in the hydrolysis liquid and subsequently measured by HPLC (Waters Acquity UPLC, Waters, MA). Percentage cellulose in the samples was measured by using the percentage glucan content, while percentage hemicelluloses was measured by adding percentage mannose, galactose, xylose and arabinose content in the biomass samples.

4.3.2.4 Fourier Transformed Infrared (FTIR) Equipment

Mid-IR beamline (01B1-1, energy range: 4000 to 400 cm^{-1}) at the Canadian Light Source Inc. (CLS, University of Saskatchewan, Saskatoon SK, Canada) was used to collect IR data of reference compounds and fine-ground sample agricultural straw in replicates of three. The beamline has a MTEC Model 300 photoacoustic cell (MTEC Photoacoustic Inc., Ames, IA) for FTIR photoacoustic spectroscopy (FTIR PAS) of bulk samples. The FTIR spectra of reference and straw samples were recorded using Globar source (silicon carbide rod). The FTIR PAS determines the absorption of radiation by samples via measuring the changes in thermal expansion of gas surrounding the sample using a microphone (McClelland et al., 2002). The reference and straw samples were filled in the sample cup and purged with dry helium to remove water vapor and CO_2 from the sample chamber. The spectrum for each sample was recorded separately by averaging 32 interferograms collected from wavenumbers of 2000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

The OPUS 6.5 (Bruker Optics Inc., Billerica, MA) software was used to record and analyze the FTIR PAS data. The software Origin (version 7.5, OriginLab, Northampton, MA) was used to plot the data.

4.3.2.5 Quantitative Analysis Using FTIR Spectra

The quantitative analysis of absorption spectrometry is based on the Bouguer-Beer-Lambert law (Sherman Hsu, 1997). According to this law, the absorbance at any frequency for a single compound in a homogenous medium is expressed as:

$A = abc$

where A is the measured sample absorbance at the given frequency, a is the molecular absorptivity at the frequency, b is the path length of source beam in the sample, and c is the concentration of the sample. The law implies that the intensities of absorption bands are linearly proportional to the concentration of each component in a homogenous mixture or solution (Sherman Hsu, 1997).

Therefore, a number of quantification parameters, which included peak height, peak area, and derivatives, were used in quantitative analysis. In this study, the authors used peak height as the quantification parameter since preliminary analysis using peak area did not produce an identifiable trend and agreeable results.

4.3.2.5.1 Peak Height Method

The spectral information of pure (100%) cellulose, hemicelluloses and lignin was developed in order to identify characteristic peaks of respective components. The distinguishable characteristic peaks of individual components were chosen to measure respective peak heights. The height of the peak (intensity of maximum absorption) was measured by calculating the difference between the peak intensity ($\overline{\nu}_{max}$) of the absorption band and the baseline ($\overline{\nu}_{min}$) (Figure 4.9). In this study, the baseline was considered at zero intensity. Therefore, peak height was equal to peak intensity ($\overline{\nu}_{max}$).

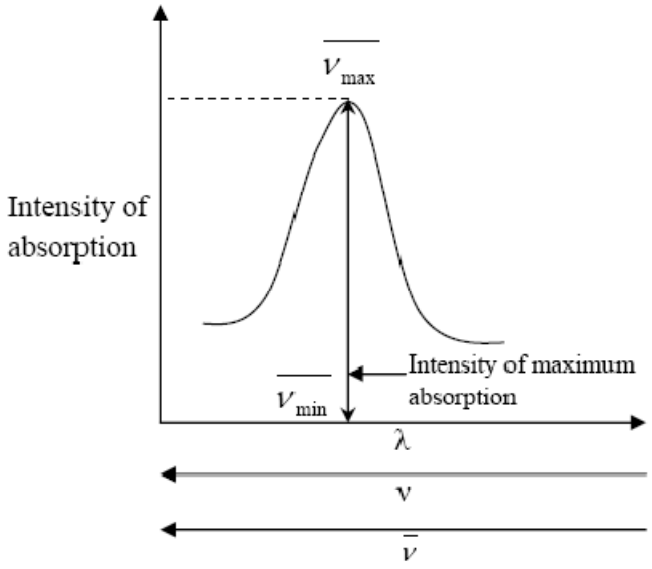


Figure 4.9: Schematic of absorption spectra (Yadav, 2005) (Note: λ is wavelength, ν is frequency and $\bar{\nu}$ is wavenumber of IR radiation).

The characteristic wavenumbers identified for pure cellulose, hemicelluloses and lignin were used as the guide to calculate the characteristic peak height for respective components in the reference compound mixtures in replicates of three. Subsequently, same characteristic wavenumbers were used to measure the characteristic peak height for cellulose, hemicelluloses and lignin components in the fine-ground non-treated and steam exploded straw sample spectra in replicates of three.

4.3.2.5.2 Data Normalization Procedure

The agricultural biomass samples FTIR spectra intensity data were corrected for any wavenumber-dependent instrumental effects through division by carbon black reference spectrum intensity. This strategy implicitly assumes that the stability of the instrumentation used is adequate to ensure reliable results, even though the sample and reference spectra were acquired at different times (Michaelian, 2005). Also, the effect of reference and sample straw bulk density was eliminated by dividing the data with respective mass of the sample contained in the PAS sample cup.

In order to further standardize the methodology, the carbon black and mass normalized FTIR data were normalized to 0 to 1 (intensity) by dividing the intensity spectra of individual biomass

samples by corresponding maximum intensity value. Hence the normalization process ensures that the model is adaptable for quantitative analysis of FTIR spectra obtained for any lignocellulosic biomass.

4.3.2.6 Statistical Analysis

The trend in variation of peak height of cellulose, hemicellulose and lignin components in the reference mixtures was correlated to their percentage composition. In addition, two replicates out of three were selected at random from the fine-ground biomass sample spectra and were included with reference mixture spectra. Regression models for cellulose, hemicelluloses and lignin were developed that has the capability to predict quantity (percentage composition) of cellulose, hemicelluloses and lignin in agricultural biomass.

The experiments were set up as completely randomized experimental design with 3 replications of FTIR tests on reference samples. The percentage composition of cellulose, hemicelluloses and lignin from chemical analysis was considered as dependent variable, while respective characteristic wavenumbers were treated as independent variables. Statistical analyses were conducted using SAS for Windows (version 9.1) (SAS, 1999). In order to understand and explain the effect of characteristic wavenumbers and their interactions on percentage cellulosic composition, the SAS general linear model (GLM) for polynomial regression and stepwise analysis were performed (SAS, 1999).

Subsequently, the characteristics peak heights for lignocellulosic composition from the third replicate of biomass sample spectrum was inserted in the developed models to predict percentage composition of lignocellulosic components in the non-treated and steam exploded barley, canola, oat and wheat straw. The average absolute difference between predicted and lab measured lignocellulosic composition was determined.

4.3.3 Results and Discussion

4.3.3.1 Lignocellulosic Composition of Agricultural Biomass

Table 4.7 shows the lignocellulosic composition of non-treated and steam exploded barley, canola, oat and wheat straw samples. In general, the cellulose, hemicelluloses and lignin content

of steam exploded straw was higher than non-treated straw. This may be due to other components (soluble lignin, loosely-bound sugars) being washed away during steam explosion, thereby leaving the proportion of insoluble lignin, cellulose and hemicellulose in the resulting dried steam exploded sample higher than the non-treated samples (i.e. higher % of dry mass).

Table 4.7: Lignocellulosic composition of non-treated and steam exploded agricultural straw

Composition (% DM)	Barley Straw		Canola Straw		Oat Straw		Wheat Straw	
	NT	SE	NT	SE	NT	SE	NT	SE
Cellulose[b]	**22.7 ± 0.9[a]**	**25.3 ± 1.8**	**22.4 ± 0.8**	**27.5 ± 1.1**	**25.4 ± 1.0**	**27.4 ± 2.4**	**27.1 ± 1.0**	**29.9 ± 1.4**
Hemicellulose[c]	**21.2 ± 0.5**	**21.0 ± 1.4**	**16.9 ± 0.5**	**20.2 ± 0.7**	**21.7 ± 0.9**	**18.8 ± 1.2**	**21.1 ± 0.5**	**19.7 ± 0.9**
a. Galactose	0.9 ± 0.0	0.7 ± 0.0	1.0 ± 0.0	0.9 ± 0.1	0.8 ± 0.0	0.7 ± 0.0	0.8 ± 0.0	0.9 ± 0.1
b. Mannose	1.6 ± 0.2	1.5 ± 0.0	2.3 ± 0.1	1.9 ± 0.4	1.4 ± 0.0	1.7 ± 0.1	1.6 ± 0.1	2.8 ± 0.2
c. Xylose	14.4 ± 0.3	15.3 ± 1.0	11.5 ± 0.5	14.3 ± 0.2	15.1 ± 0.8	13.3 ± 1.0	14.9 ± 0.4	13.5 ± 0.4
d. Arabinose	4.4 ± 0.2	3.5 ± 0.5	2.0 ± 0.1	3.2 ± 0.0	4.4 ± 0.2	3.1 ± 0.2	3.9 ± 0.1	2.6 ± 0.2
Total Lignin[d]	**21.0 ± 0.6**	**21.6 ± 0.6**	**19.6 ± 0.6**	**22.3 ± 0.2**	**19.5 ± 0.6**	**23.7 ± 0.2**	**22.5 ± 0.7**	**24.2 ± 0.3**
a. Soluble Lignin	1.6 ± 0.1	1.4 ± 0.1	1.6 ± 0.1	1.2 ± 0.1	1.5 ± 0.1	1.3 ± 0.1	1.4 ± 0.0	1.0 ± 0.1
b. Insoluble Lignin	19.4 ± 0.6	20.2 ± 0.6	18.0 ± 0.6	21.1 ± 0.1	17.9 ± 0.7	22.4 ± 0.1	21.0 ± 0.7	23.3 ± 0.4

DM – Dry Matter; NT – Non-Treated; SE – Steam Exploded;

[a] Average and standard deviation of 3 replicates at 95% confidence interval;

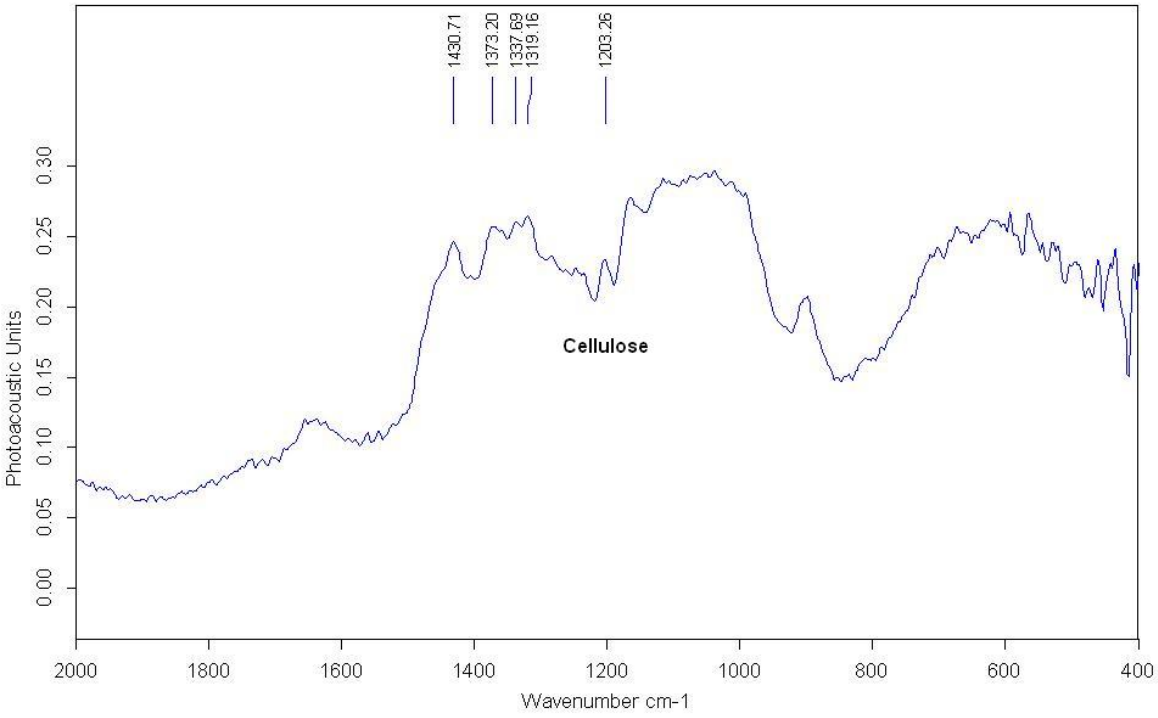
[b]%Cellulose = %glucan;

[c]%Hemicellulose = %(mannose + galactose + xylose + arabinose);

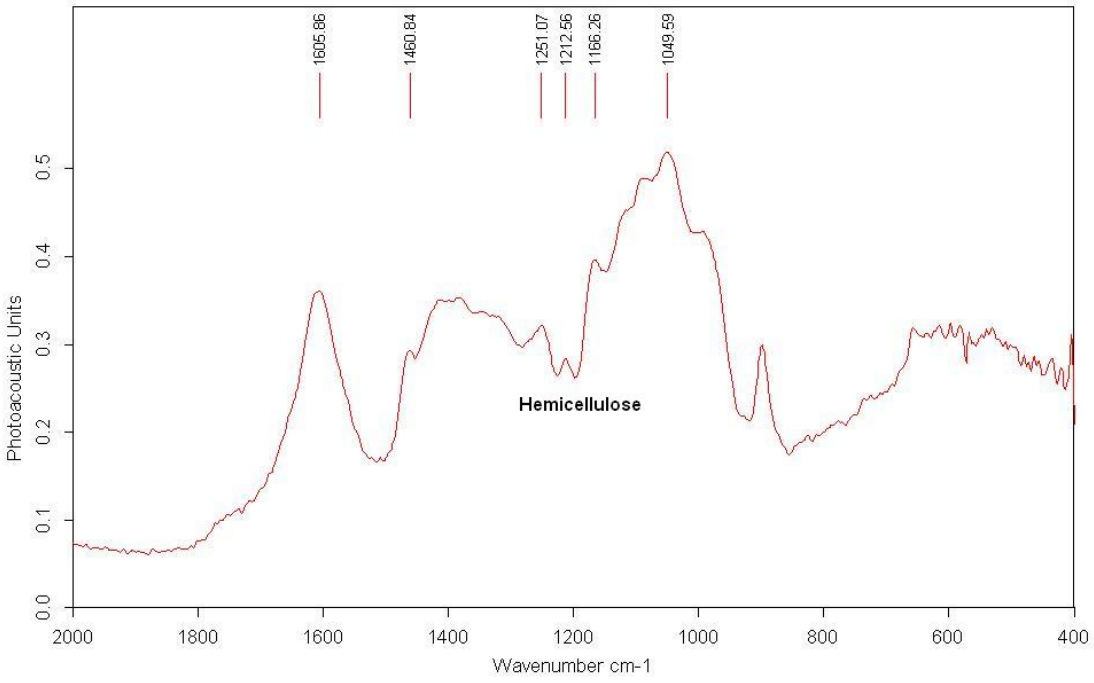
[d]%Total Lignin = %(soluble lignin + insoluble lignin).

4.3.3.2 Reference Material Spectra

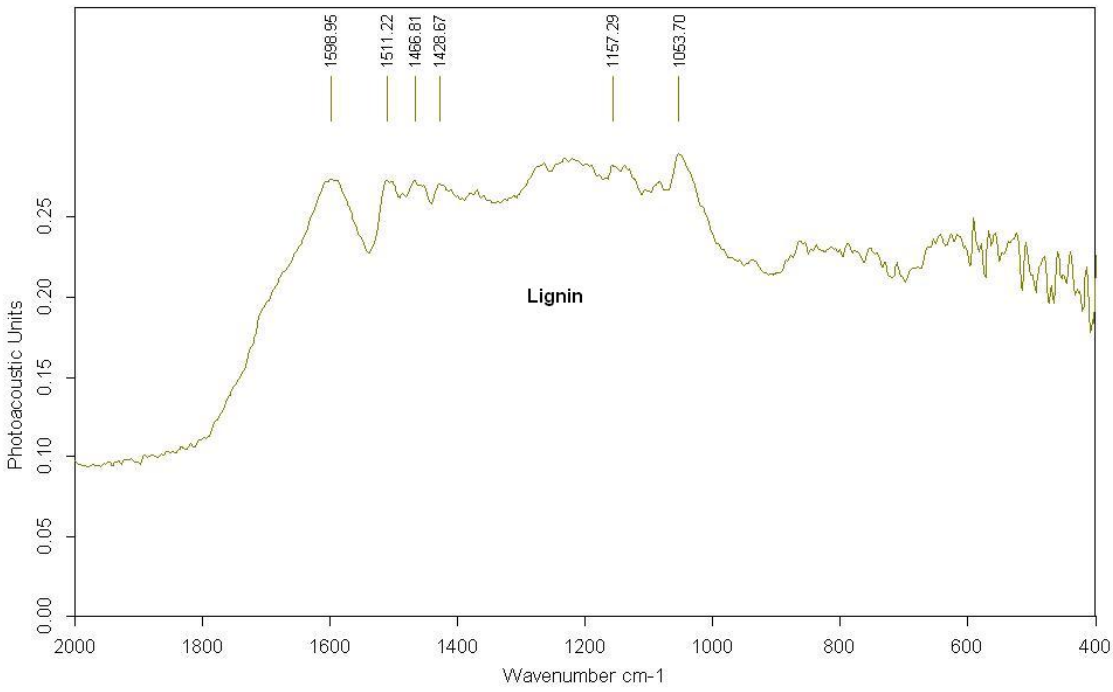
Figure 4.10 represents the FTIR PAS spectra of pure cellulose, hemicellulose and lignin powder in the range of 2000 to 400 cm^{-1}. The characteristic/ prominent peaks for cellulose, hemicellulose and lignin, and their peak assignments are provided in Table 4.8. The cellulose spectrum had five distinct peaks at wavenumbers of 1431, 1373, 1338, 1319 and 1203 cm^{-1} (Figure 4.10a). Similarly, hemicellulose (xylan) had prominent peaks at wavenumbers of 1606, 1461, 1251, 1213, 1166 and 1050 cm^{-1} (Figure 4.10b). The lignin spectrum showed characteristic peaks at wavenumber of 1599, 1511, 1467, 1429, 1157 and 1054 cm^{-1} (Figure 4.10c).



(4.10a) Cellulose 100%



(4.10b) Hemicellulose 100%



(4.10c) Lignin 100%

Figure 4.10: FTIR PAS spectra of pure cellulose (microcrystalline powder), hemicelluloses (xylan from birch wood) and lignin (hydrolytic) powders

Table 4.8: Characteristic/ prominent peaks of pure cellulose, hemicellulose and lignin, and their peak assignments.

Wavenumbers (cm^{-1})	Cellulose 100%	Hemicellulose 100%	Lignin 100%	Peak Assignment
1650-1600	--	1606	--	1600 – quadrant ring stretching (aromatic lignin) (Colthup et al., 1990; Yu et al., 2007); 1600-1610 – aromatic skeletal vibration (Yu et al., 2007; Pandey, 1999); 1635 – carbonyl stretching conjugate with aromatic rings (Cyran and Saulnier, 2007)
1600-1550	--	--	1599	1595 – very strong aromatic ring stretch, aromatic C-O stretch (Revol, 1982; Stewart et al., 1995); 1595 – phenylpropanoid polymer (Himmelsbach and Akin, 1998); 1595 – aromatic skeletal vibrations plus C=O stretch (Lin and Dence, 1991)
1550-1500	--	--	1511	1510 – semicircle ring stretching (aromatic lignin) (Colthup et al., 1990; Yu et al., 2007; Yu, 2005), 1510 – phenylpropanoid polymer (Himmelsbach and Akin, 1998); 1510 – very strong aromatic ring stretch, aromatic C-O stretch (Revol, 1982; Stewart

				et al., 1995); 1513 – aromatic C=C stretch (Sun et al., 2005); 1514 – semi-circle stretch of para-substitute benzene rings (Budevska, 2002; Lin-Vein et al., 1991); 1550 – protein (Budevska, 2002)
1500-1450	--	1461	1467	1462 – C-H deformation (methyl and methylene) (Pandey, 1999)
1450-1400	1431	--	1429	1420 – weak C-O stretching (Yu et al., 2007; Wetzel et al., 1998); 1430 – CH_2 in-plane bending vibrations (Schulz and Baranska, 2007; Wilson et al., 2000); 1433 – aromatic C=C stretch (Sun et al., 2005)
1400-1350	1373	--	--	1370 – weak C-O stretching (Yu et al., 2007; Wetzel et al., 1998); 1380 – C-H symmetric and asymmetric deformation (Sun et al., 2005); 1382 – C-O stretch (Xu et al., 2007)
1350-1300	1319, 1338	--	--	1335 – weak C-O stretching (Yu et al., 2007; Wetzel et al., 1998); 1336 – C-H ring in-plane bending vibrations (Schulz and Baranska, 2007; Wilson et al., 2000)
1300-1250	--	1251	--	1250 – Acetylated Hemicellulose (Himmelsbach and Akin, 1998)
1250-1200	1203	1213	--	1246 – weak C-O stretching (Yu et al., 2007; Wetzel et al., 1998); 1246 – Hemicellulose (Budevska, 2002; Yu et al., 2007); 1250 – Acetylated Hemicellulose (Himmelsbach and Akin, 1998); 1250 – acetylated hemicelluloses (Budevska, 2002)
1200-1150	--	1166	1157	1160 – glycosidic linkage (Robert et al., 2005); 1162 – C-O-C ring vibrational stretching (Schulz and Baranska, 2007; Wilson et al., 2000)
1100-1050	--	--	1054	1078 – β(1-3) polysaccharide (Szeghalmi et al., 2007); 1098 – weak absorbance (Stewart et al., 1995)
1050-1000	--	1050	--	1035 – C-O, C=C and C-C-O vibrational stretching (Schulz and Baranska, 2007; Wilson et al., 2000); 1045 – C-OH bending (Cyran and Saulnier, 2007; Robert et al., 2005; Agarwal and Kawai, 2003); 1018 – galactomannans (Szeghalmi et al., 2007); 1025 – non-structural CHO (Yu et al., 2007)

4.3.3.3 Quantitative Analysis

After following the data normalization process described in section 4.3.2.5.2, the effect of characteristic wavenumbers and their interaction on percentage composition of cellulose, hemicelluloses and lignin were analyzed using SAS GLM procedure and was considered significant when the value of $t \leq 0.05$. In addition, polynomial regression models having highest R^2 values were obtained (Table 4.9). Also, the stepwise method in the regression procedure was used to determine wavenumbers and interactions having significant affect on lignocellulosic

composition of biomass in decreasing order and accordingly organized in the regression equations (Table 4.9).

Table 4.9: Summary of statistical analysis using the Proc GLM method for polynomial regression analysis

Significant Wavenumbers and Interactions	Estimated Coefficients	R^2 value	Root Mean Square Error	Mean Absolute Deviation
$\%Cellulose = -135.10 + 781.35(PH\_1319) - 795.57(PH\_1431) - 135.26(PH\_1203) + 436.11(PH\_1338) - 94.24(PH\_1373)$				
Intercept	-135.10	0.89	8.39	7.5
1319	781.35			
1431	-795.57			
1203	-135.26			
1338	436.11			
1373	-94.24			
$\%Hemicellulose = 1638.72 - 2581.71(PH\_1251 \times PH\_1461) - 1260.90(PH\_1213) - 2518.05(PH\_1166) + 1573.69(PH\_1213 \times PH\_1251) + 118.74(PH\_1050) + 3128.51(PH\_1166 \times 1251) + 2179.65(PH\_1461) + 92.36(PH\_1606) - 2294.15(PH\_1251) - 59.29(PH\_1461 \times PH\_1606)$				
Intercept	1638.72	0.99	2.76	2.5
1251*1461	-2581.71			
1213	-1260.90			
1166	-2518.05			
1213*1251	1573.69			
1050	118.74			
1166*1251	3128.51			
1461	2179.65			
1606	92.36			
1251	-2294.15			
1461*1606	-59.29			
$\%Lignin = 7110.87 + 388.32(PH\_1511 \times PH\_1599) - 16440.93(PH\_1467) + 447.36(PH\_1599)^2 + 19572.82(PH\_1157 \times PH\_1467) + 18374.36(PH\_1157) + 15659.98(PH\_1054 \times PH\_1429) - 4952.80(PH\_1157 \times PH\_1599) + 800.20(PH\_1511) - 3032.75(PH\_1429)^2 - 11269.16(PH\_1429) - 948.04(PH\_1511)^2 + 3444.69(PH\_1599) - 12344.90(PH\_1054) - 16689.44(PH\_1157)^2$				

Intercept	7110.87	0.98	3.89	3.8
1511*1599	388.32			
1467	-16440.93			
1599*1599	447.36			
1157*1467	19572.82			
1157	18374.36			
1054*1429	15659.98			
1157*1599	-4952.80			
1511	800.20			
1429*1429	-3032.75			
1429	-11269.16			
1511*1511	-948.04			
1599	3444.69			
1054	-12344.90			
1157*1157	-16689.44			

Note: PH represents characteristic maximum Peak Height (Photoacoustic Units) at respective wavenumbers

4.3.3.4 Sample Material Spectra

The characteristic peak heights of cellulose, hemicellulose and lignin for the third replicate of barley, canola, oat and wheat straw samples were determined by using the wavenumbers provided in Table 4.9 and following the procedure described in the materials and methods (section 4.3.2.5.1). The peak height values were subsequently used to predict the percentage of lignocellulosic composition in the corresponding agricultural straw samples using the SAS GLM procedure (Table 4.9). The average absolute difference in predicted and lab based measured percentage of cellulose, hemicellulose and lignin in agricultural biomass was 7.5%, 2.5%, and 3.8%, respectively (Table 4.9). The error in prediction could be attributed to larger grind size of sample material as compared to reference material (Agarwal and Kawai, 2003). Sherman Hsu (1997) indicated that the deviation from the Bouguer-Beer-Lambert law often occurs in infrared spectroscopy. These deviations stem from both instrumental and sample effects. Assuming negligible instrumental effect, the sample effect will include chemical reactions and molecular interactions such as hydrogen bonding (Sherman Hsu, 1997). In addition, the reference materials (pure samples and their mixtures) used in the present experiments were obtained commercially, which were derived from different biomass sources. Therefore, pure cellulose, hemicellulose

and lignin derived from agricultural straw should be considered for future tests, which may further reduce the percentage difference in measured and predicted values.

4.4 Conclusions

The IR and Raman spectromicroscopic methods have the potential to determine the structural characteristics and chemical compound distribution in agricultural (lignocellulosic) biomass enabling it suitable for biorefineries. However, both these methods have their own advantages and drawbacks, and should be used as complementary techniques. By combining spectroscopy with microscopy molecular information can be obtained with great spatial resolution at the microscopic level.

The literature review of lignocellulosic biomass have indicated that IR and Raman spectromicroscopy could be used successfully to study the chemical structure and spatial distribution of cellulose, hemicellulose and lignin in various agricultural biomasses as applied to food, feed, biocomposite, textile, and paper and pulp industries. However, no published research has been found that could address the need to determine the structural characteristics and chemical components distribution in agricultural biomass using IR and Raman spectroscopic methods enabling it suitable for biorefineries. There is a need to initiate studies that could develop information on the spatial origin and distribution of the components of interest when subjected to various pre-processing and pre-treatment methods at microscopic level as opposed to quantification of chemical composition of biomass by relying on the separation of the components of interest.

In addition to the literature review, a novel procedure to quantitatively predict lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat straw, which could be easily extended for any form of lignocellulosic biomass using FTIR spectroscopy was successfully developed. The FTIR quantitative analysis of mixtures of pure cellulose, hemicelluloses and lignin, and measured lignocellulosic composition of agricultural biomass samples resulted in predictive regression equations having R^2 values of 0.89, 0.99 and 0.98, respectively. The average absolute difference in predicted and measure cellulose, hemicellulose and lignin in agricultural biomass was 7.5%, 2.5%, and 3.8%, respectively.

Chapter 5

5. Compression and Compaction Characteristics of Non-Treated and Steam Exploded Agricultural Straw Grinds

A similar version of this chapter has been published in the journal of Applied Engineering in Agriculture. This version is considerably longer and includes compression models, experimental details and results on both non-treated and steam exploded agricultural biomass:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2010. Compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw grinds. *ASABE Journal of Applied Engineering in Agriculture*, 26(4): 617-632.

In this article, a comprehensive review of various compression models was performed and preliminary study on compression behavior of selected non-treated ground agricultural biomass was accomplished. The article was published in the CIGR Ejournal and presented in Appendix B of this thesis:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2009. Compression characteristics of selected ground agricultural biomass. *Agricultural Engineering International: the CIGR Ejournal*, Manuscript 1347, XI(June): 1-19.

In this article, a detailed literature review on the effect of independent variables such as moisture content, grind size, and pressures on dependent variables such as pellet density, durability and specific energy was performed. In addition, preliminary compaction experiments were performed on non-treated barley, canola, oat and wheat straw. The article was published in the journal of Biosystems Engineering and presented in Appendix C of this thesis:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2009. Compaction characteristics of barley, canola, oat and wheat straw. Biosystems Engineering, 104: 335-344.

During the course of Ph.D. research, the outcomes of literature review on compression models, analysis of preliminary experiments, and analysis of comprehensive data on compression and compaction behaviour of non-treated and steam exploded agricultural straw were in-part also presented and published in four national and international conferences:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2010. Compression characteristics of agricultural biomass subject to pre-treatment. 2nd Annual General Meeting, Cellulosic Biofuel Network Meeting, Agricultural and Bioproducts Innovation Program, Ottawa, ON, Poster No. 11, March 11-12, and Agricultural Biorefinery Innovation Network, Agricultural and Bioproducts Innovation Program, London, ON, March 15-16.
- Adapa, P.K., L.G. Tabil, G.J. Schoenau and D. Nelson. 2009. Compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw grinds. ASABE/CSBE North Central Intersectional Conference, Student Union, South Dakota State University, Brookings, USA, Paper No. SD09-900, September 18-19. St. Joseph, MI: ASABE.
- Adapa, P.K., D. Nelson, L.G. Tabil and G.J. Schoenau. 2009. Compaction characteristics of non-treated and steam exploded barley, canola, oat and wheat straw grinds. ASABE/CSBE North Central Intersectional Conference, Student Union, South Dakota State University, Brookings, USA, Paper No. SD09-800, September 18-19. St. Joseph, MI: ASABE.
- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2009. Pelleting characteristics of selected agricultural biomass – density and energy models. Biofuels & Bioenergy - A Changing Climate, IEA Bioenergy Conference, Vancouver, Poster No. 15, July 23-26.

Contribution of Ph.D. Candidate

Baseline data and correlations for pellet density and specific energy required for pelleting with applied pressure and hammer mill screen size for both non-treated and steam exploded straw

grinds were developed. A relative comparison of non-treated and steam exploded agricultural biomass was performed that could be used by the biofuel pellet manufacturers to optimize various variables during the pelleting process. In addition, compression characteristics of both non-treated and steam exploded straw grinds were studied to understand the fundamental mechanism underlying the densification process. Literature review, designing of experiments, data analysis, and writing of journal articles were performed by Phani Adapa, while Dr. Lope Tabil and Dr. Greg Schoenau suggested the approach to data analysis, provided editorial input and reviewed the experimental process. Ms. Dallas Nelson provided technical assistance during single-pellet experimental process.

Contribution of these Papers to Overall Study

Knowledge Gap: Some previous work had been reported on mechanical properties of ground non-treated barley and wheat straw, and steam exploded wheat straw as a feedstock for biofuel industry. However, no studies have been found in the area of densification of steam exploded agricultural biomass. In addition, a relative comparison of non-treated and steam exploded agricultural biomass is required to determine the feasibility of establishing a modified desification process. Therefore, the objectives of this study were: a) to determine the effect of pressure and biomass grind size on density and specific energy requirements for compacting non-treated and steam exploded barley, canola, oat and wheat straw grinds; and b) to determine the pressure-volume and pressure-density relationship to analyze the compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw using three compression models, namely: Jones (1960), Cooper-Eaton (1962), and Kawakita-Ludde (1971), models.

Justification: Densification of biomass into durable compacts is an effective solution to meet the requirement of raw material for biofuel production. The compression characteristics of ground agricultural biomass vary under various applied pressures. It is important to understand the fundamental mechanism of the biomass compression process, which is required to design an energy efficient compaction equipment to mitigate the cost of production and enhance the quality of the product. To a great extent, the strength of manufactured compacts depends on the physical forces that bond the particles together. These physical forces are generated in three different

forms during compaction operations: a) thermal; b) mechanical; and c) atomic forces. To customize and manufacture high quality products that can withstand various forces during transportation and handling, it is essential to predict desirable and dependent quality parameters (density and durability) with respect to various independent variables (pre-treatment, grind size, applied pressure, hold time, die temperature, and moisture content). In addition, the specific energy requirements of manufacturing biomass pellets should be established, which can assist in determining the economic viability of densification process.

5.1 Abstract

Compaction of low bulk density agricultural biomass is a critical and desirable operation for sustainable and economic availability of feedstock for biofuel industry. A comprehensive study of the compression characteristics (density of pellet and total specific energy required for compression) of ground non-treated and steam exploded barley, canola, oat and wheat straw obtained from three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm at 10% moisture content (wb) was conducted. Four preset pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were applied using an Instron testing machine to compress samples in a cylindrical die. Ground steam exploded barley straw at screen sizes of either 3.2 or 1.6 mm produced high density compacts, while ground steam exploded canola, oat and wheat straw at screen sizes of 6.4, 3.2 or 1.6 mm produced high density compacts. Steam exploded barley straw for 3.2 mm at 138.9 MPa produced compacts having 13% higher density and consumed 19% lower total specific energy compared to non-treated straw. Steam exploded canola straw for 1.6 mm at 138.9 MPa produced compacts having 13% higher density and consumed 22% higher total specific energy compared to non-treated straw. Steam exploded oat straw for 3.2 mm at 94.7 MPa produced compacts having 19% higher density and consumed 13% higher total specific energy compared to non-treated straw. Steam exploded wheat straw for 6.4 mm at 138.9 MPa produced compacts having 17% higher density and consumed 17% higher total specific energy compared to non-treated straw. Three compression models, namely: Jones model, Cooper-Eaton model, and Kawakita-Ludde model were considered to determine the pressure-volume and pressure-density relationship of non-treated and steam exploded straws. Kawakita-Ludde model provided the best fit to the experimental data having R^2 values of 0.99 for non-treated straw and 1.00 for steam exploded biomass samples. The steam exploded straw had higher porosity than non-treated

straw. In addition, the steam exploded straw was easier to compress since it had lower yield strength or failure stress values compared to non-treated straw.

5.2 Introduction

Compaction of low bulk density agricultural biomass is a critical and desirable operation for sustainable and economic availability of feedstock for biofuel industry. Due to its high moisture content, irregular shape and sizes, and low bulk density, biomass is very difficult to handle, transport, store, and utilize in its original form (Sokhansanj et al., 2005). Compacted biomass has uniform shape and size, can be easily handled using standard handling and storage equipment (Mani et al., 2003), and easily adopted in direct-combustion or co-firing with coal, gasification, pyrolysis, and in other biomass-based conversions (Kaliyan and Morey, 2006a). Upon densification, many agricultural biomass materials, especially those from straw, result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture. This is due to lack of complete understanding on the natural binding characteristics of the components that make up biomass (Sokhansanj et al., 2005).

The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). It is postulated that by disrupting the lignocellulosic matrix of biomass materials via steam explosion pretreatment, the compression and compaction characteristics can be improved (Shaw, 2008). Zandersons et al. (2004) stated that activation of lignin and changes in the cellulosic structure during the steam explosion process facilitate the formation of new chemical bonds. Lam et al. (2008) reported that the quality (durability) of compacts produced from steam exploded sawdust was 20% higher than non-treated sawdust.

The compression characteristics of ground agricultural biomass vary under various applied pressures. It is important to understand the fundamental mechanism of the biomass compression process, which is required to design an energy efficient compaction equipment to mitigate the cost of production and enhance the quality of the product (Mani et al., 2004). To a great extent, the strength of manufactured compacts depends on the physical forces that bond the particles together (Tabil and Sokhansanj, 1996). These physical forces are generated in three different

forms during compaction operations: a) thermal; b) mechanical; and c) atomic forces (Adapa et al., 2002).

Pellets are formed by subjecting the biomass grinds to high pressures, wherein the particles are forced to agglomerate. It is generally accepted that the compression process is categorized in several distinct stages and difficult to let one simple monovariate equation to cover the entire densification region (Sonnergaard 2001). Compression of grinds is usually achieved in three stages (Holman 1991). In the first stage, particles rearrange themselves under low pressure to form close packing. The particles retain most of their original properties, although energy is dissipated due to inter-particle and particle-to-wall friction. During the second stage, elastic and plastic deformation of particles occurs, allowing them to flow into smaller void spaces, thus increasing inter-particle surface contact area and as a result, bonding forces like van der Waal forces become effective (Rumpf 1962; Sastry and Fuerstenau 1973; Pietsch 1997). Brittle particles may fracture under stress, leading to mechanical interlocking (Gray 1968). Finally, under high pressure the second stage of compression continues until the particle density of grinds has been reached. During this phase, the particles may reach their melting point and form very strong solid bridges upon cooling (Ghebre-Sellassie 1989). Figure 5.1 shows the deformation mechanisms of powder particles under compression (Comoglu 2007; Denny 2002).

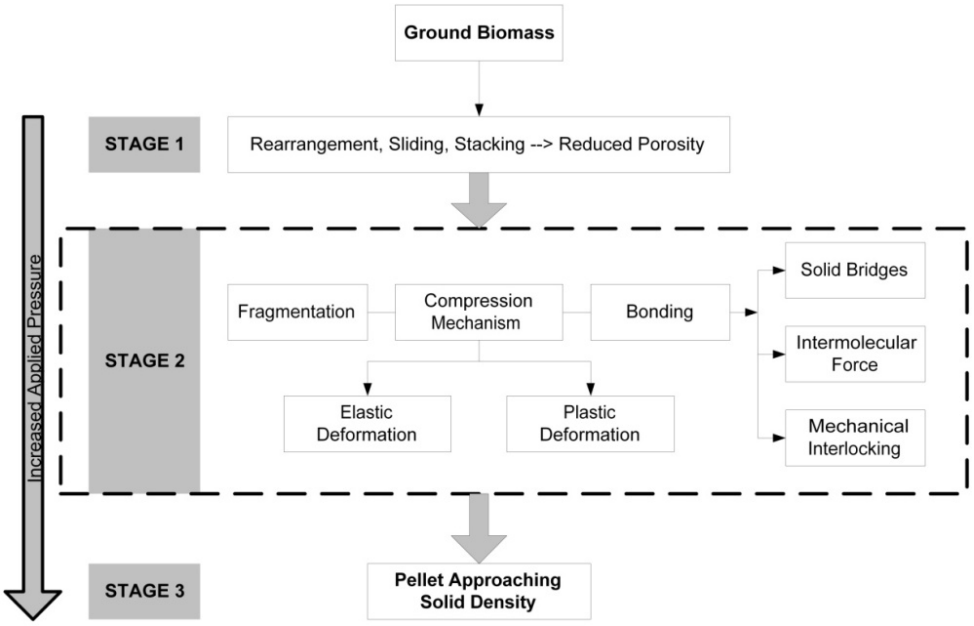


Figure 5.1: The defromation mechanisms of powder particles under compression (Comoglu, 2007; Denny, 2002)

The moisture in biomass both acts as a facilitator of natural binding agents and a lubricant (Kaliyan and Morey, 2006a). According to Obernberger and Thek (2004), production of high quality pellets is possible only if the moisture content of the feed is between 8 and 12% (wb). Moisture contents above or below this range would lead to lower quality pellets. Kaliyan and Morey (2006b and 2007) observed no significant difference in briquette densities for 10 and 15% moisture contents at an applied pressure of 100 MPa for corn stover; however, the densities decreased by 30-40% with an increase in moisture from 10 to 15% at a pressure of 150 MPa. A similar trend of decrease in density with increasing moisture levels was reported by Mani et al. (2002 and 2006a) for pellets made from wheat straw, barley straw, corn stover, and switchgrass. Shaw (2008) observed that at lower loads, the compact density was higher at 15% (wb); however, as the load was increased (from 1000 N to 4000 N), the compacts made from 9% (wb) moisture produced denser compacts. Shaw and Tabil (2007) also reported similar results and concluded that lower moisture materials produce denser compacts.

Mani et al. (2002 and 2004) reported an increase in pellet densities from 5 to 16% when pelleting corn stover grind obtained from the hammer mill screen sizes of 3.2, 1.6 and 0.8 mm. Similar results were reported by Kaliyan and Morey (2006b) of an increase in briquette densities from 5 to 10% when the geometric mean particle size of corn stover grinds decreased from 0.80 to 0.66 mm. For switchgrass, reducing the geometric mean particle size from 0.64 to 0.56 mm did not show any significant impact on the briquette density (Kaliyan and Morey 2006b). The observations have been echoed by Mani et al. (2002) who were unable to show any trend in variation in switchgrass pellet densities made with grinds having geometric mean particle size in the range of 0.25 to 0.46 mm.

Mani et al. (2006a) successfully densified corn stover into dense briquettes having density of 650-950 kg/m^3 and the specific energy required to compress and extrude corn stover was in the range of 12-30 MJ/t. The extrusion (frictional) energy required to overcome the skin friction was roughly half of the total energy. Mewes (1959) showed that roughly 40% of the total applied energy was used to compress the materials (straw and hay) and the remaining 60% was used to overcome friction. Faborode and O'Callaghan (1987) studied the energy requirement for compression of fibrous agricultural materials. They reported that chopped barley straw at 8.3% (wb) moisture content consumed 28-31 MJ/t of energy, while un-chopped material consumed 18-

27 MJ/t. Kaliyan and Morey (2006b) reported that at pressure of 150 MPa, 10% moisture content and a preheat temperature of 100^{o}C, and decreasing the particle size of corn stover grind from 0.8 to 0.66 mm did not result in significant change in specific energy consumption from 189 MJ/t. Whereas for switchgrass briquetting, decreasing the particle size from 0.64 to 0.56 mm slightly decreased the specific energy consumption from 189 to 187 MJ/t. Shaw (2008) reported that between 95 and 99% of the total specific energy was required to compress the grinds, whereas between 1 and 5% of the total specific energy was required to extrude the compact in single compact tests. Shaw (2008) also reported that the mean values of specific compression energy ranged from 7.2 (pretreated wheat straw using steam explosion) to 39.1 MJ/t (wheat straw).

Some previous work had been reported by Mani et al. (2006a and 2006b) on mechanical properties of ground barley and wheat straw and by Shaw (2008) on ground non-treated and steam exploded wheat straw as a feedstock for biofuel industry. There is a dearth of knowledge in the area of densification of steam exploded agricultural biomass. In addition, a relative comparison of non-treated and steam exploded agricultural biomass is required to determine the feasibility of establishing a modified desification process. Therefore, the objectives of this study were:

1. To determine the effect of pressure and biomass grind size on density and specific energy requirements for compacting non-treated and steam exploded barley, canola, oat and wheat straw grinds.

2. To determine the pressure-volume and pressure-density relationship to analyze the compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw using three compression models, namely: Jones (1960), Cooper-Eaton (1962), and Kawakita-Ludde (1971), models.

5.3 Compression Models

A majority of compression models applied to pharmaceutical and biomass materials have been discussed and reviewed in detail by Adapa et al. (2002), Denny (2002) and Mani et al. (2003).

5.3.1 Jones Model

Jones (1960) expressed the density-pressure data of compacted metal powder in the form of equation 5.1.

$$\ln \rho = \boldsymbol{m} \ln \boldsymbol{P} + \boldsymbol{b} \tag{5.1}$$

where, ρ is bulk density of compact powder mixture, kg/m^3, P is applied compressive pressure, MPa; *m* and *b* are model constants.

The constants *b* and *m* are determined from the intercept and slope, respectively, of the extrapolated linear region of the plot of *ln(ρ)* vs *ln(P)*. The constant *m* has been shown to be equal to the reciprocal of the mean yield pressure required to induce plastic deformation (York and Pilpel, 1973). A large *m* value (low yield pressure) indicates the onset of plastic deformation at relatively low pressure, thus, the material is more compressible.

5.3.2 Cooper-Eaton Model

Cooper-Eaton (1962) studied the compaction behavior of four ceramic powders. In each case it was assumed that compression is attained by two nearly independent probabilistic processes, namely, the filling of voids having equal size as particles and filling of voids smaller than particles. Based on these assumptions, the following equation was given:

$$\frac{\boldsymbol{V_o - V}}{\boldsymbol{V_o - V_S}} = \boldsymbol{a}_1 \boldsymbol{e}^{-\frac{\boldsymbol{k}_1}{\boldsymbol{P}}} + \boldsymbol{a}_2 \boldsymbol{e}^{-\frac{\boldsymbol{k}_2}{\boldsymbol{P}}} \tag{5.2}$$

where, V_0 = volume of compact at zero pressure, m^3; V = volume of compact at pressure P, m^3; V_S = void free solid material volume, m^3; a_1, a_2, k_1, and k_2 = Cooper-Eaton model constants.

The difficulty in practical use of the equation is the assignment of some physical significance to the constant parameters of this equation. In addition, another drawback of this model is its applicability to only one-component system (Comoglu, 2007).

5.3.3 Kawakita-Ludde Model

Kawakita and Ludde (1971) performed compression experiments and proposed an equation for compaction of powders based on observed relationship between pressure and volume (equation 5.3).

$$\frac{\boldsymbol{P}}{\boldsymbol{C}} = \frac{1}{\boldsymbol{ab}} + \frac{\boldsymbol{P}}{\boldsymbol{a}} \tag{5.3}$$

Where,

$$\boldsymbol{C} = \frac{\boldsymbol{V}_0 - \boldsymbol{V}}{\boldsymbol{V}_0}$$

C = degree of volume reduction or engineering strain; *a* and *b* = Kawakita-Ludde model constants related to characteristic of the powder.

The linear relationship between *P/C* and *P* allows the constants to be evaluated graphically. This compression equation holds true for soft and low bulk density powders (Denny, 2002; Kawakita and Ludde, 1971), but particular attention must be paid on the measurement of the initial volume of the powder. Any deviations from this expression are sometimes due to fluctuations in the measured value of V_0. The constant *a* is equal to the values of $C = C_\infty$ at infinitely large pressure *P*.

$$\boldsymbol{C}_\infty = \frac{\boldsymbol{V}_0 - \boldsymbol{V}_\infty}{\boldsymbol{V}_0}$$

Where, V_∞ = net volume of the powder, m^3.

It has been reported that the constant *a* is equal to the initial porosity of the sample, while constant *1/b* is related to the failure stress in the case of piston compression (Mani et al., 2004).

5.4 Materials and Methods

5.4.1 Agricultural Biomass

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for the experiments. The straw samples were acquired in small square bale form (typically having dimensions of 0.45 x 0.35 x 1.00 m) during the summer of 2008 from a farmer in the Central Butte area of Saskatchewan, Canada.

The initial moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (wb), respectively. The agricultural biomass was stored under a tarpaulin cover during the winter of 2008 (approximately for 7 months). During this period, the moisture content of barley, canola, oat and wheat straw was increased to 13.5, 15.1, 13.1 and 15.6% (wb), respectively.

All of the baled straw samples were chopped using a chopper, which was fabricated in the Bioprocessing Lab, Department of Agricultural and Bioresource Engineering, University of Saskatchewan, Canada. The biomass chopper was equipped with a feed hopper and a pair of rollers to feed the material to the chopping blades. The feed rate of biomass to the blades was dependent on the roller speed. After a few preliminary trials, the rollers were set to rotate at 50 rpm in order to avoid material clogging. Each of the six chopper blades were inclined at an angle of 14^{o} (with respect to horizontal axis of rotation) to deliver shearing effect on the biomass and were set to rotate at 460 rpm.

The chopped biomass was subsequently ground using a hammer mill (Serial no. 6M13688; 230 Brookdale, St. Maywood, NJ) having 22 swinging hammers, attached to a shaft powered by a 1.5 kW electric motor. The shaft was allowed to rotate at 3800 rpm. Four screen sizes of 30, 6.4, 3.2 and 1.6 mm were used to grind the non-treated biomass. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK) having a 9 A suction fan rotating at 3500 rpm was connected to the outlet of the hammer mill to control dust during operation, provide flowability of chopped biomass through the hammer mill, and collect the ground biomass using a cyclone system. A portion (25 kg) of each of the biomass ground in the hammer mill using 30 mm screen was sent to FPInnovations in Quebec City, Quebec for steam explosion pretreatment.

5.4.2 Steam Explosion of Agricultural Biomass

The steam explosion of ground straw obtained using 30 mm hammer mill screen size was performed at the pilot-scale continuous steam explosion plant of FPInnovations, Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized refiner having a plate gap of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive was set to operate at 2000 rpm. The throughput of the equipment can vary between 50 and 200 kg of dried material per hour, depending on the bulk density of the raw material and the desired final particle size of the steam exploded material. The feed rate of agricultural straw into the digester was controlled using a plug screw feeder. The digester was operated at 180^{o}C (steam pressure of 900 kPa) for 4 min to perform steam explosion pretreatment of the agricultural biomass. A flash tube convective dryer having 90 m long tube was used to dry the steam exploded barley, canola, oat and wheat straw at an average moisture content of 70.1, 80.7, 76.7 and 81.0% (wb) to approximately an average moisture content of 12.2, 13.6, 12.0 and 12.0% (wb), respectively. The direct heating of air was performed using 1172 kW (4 million BTU/h) natural gas burner, which has variable control to operate at different temperatures.

During the transportation of steam exploded material from Quebec City, Quebec to Saskatoon, Saskatchewan, the average moisture content of steam exploded barley, canola, oat and wheat straw was reduced to 7.8, 6.2, 6.8 and 7.0 % (wb), respectively. The steam exploded material was further ground in a hammer mill using three screen sizes of 6.4, 3.2 and 1.6 mm following the procedure described in the previous section.

Figure 2.3 (Chapter 2) shows the photograph of non-treated (at hammer mill screen size of 30 mm) and steam exploded barley, canola, oat and wheat straw grinds. It could be noticed from the figure that steam exploded straw has significantly lower bulk density and may have lower flowability compared to non-treated straw.

5.4.3 Moisture Content

The moisture content of baled straw and steam exploded biomass was determined using ASAE S358 (2006a), where 25 g of material was oven-dried at 103^{o}C for 24 h. The moisture content of ground straw at hammer mill screen size of 6.4, 3.2 and 1.6 mm was determined using AACC

Standard 44-15A (2005), where 2-3 g of material was oven-dried at 130^{o}C for 90 min. All of the moisture content tests were performed in replicates of three.

5.4.4 Particle Size Analysis

The geometric mean particle diameter of ground non-treated and steam exploded agricultural straw samples was determined using ASAE Standard S319 (2006b). Due to the low bulk density of steam exploded straw, only 50 g of ground sample was placed on a stack of sieves arranged from the largest to the smallest opening. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used for particle size analysis. The sieve series selected were based on the range of particles in the samples. For grinds from 6.4 mm hammer mill screen opening, U.S. sieve numbers 10, 16, 20, 30, 50 and 70 (sieve opening sizes: 2.000, 1.190, 0.841, 0.595, 0.297 and 0.210 mm, respectively) were used. For grinds from 3.2 and 1.6 mm hammer mill screen openings, U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively) were used. A 10 min sieve shaking time was used as suggested in the ASAE Standard S319. The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated in replicates of three for each straw samples.

5.4.5 Bulk and Particle Density

Bulk density of hammer mill ground non-treated and steam exploded agricultural straw at three screen sizes of 6.4, 3.2 and 1.6 mm was determined by carefully filling a standard 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB) with sample. After filling every third portion of the container with ground straw sample, it was tapped on a wooden table for approximately 10 times to allow the material to settle down. After completely filling the container, excess material at the top was removed by moving a steel roller in a zig-zag pattern. The mass per unit volume gave the bulk density of the biomass in kg/m^3. A gas multi-pycnometer (QuantaChrome, Boynton Beach, FL) was used to determine the particle density of the hammer mill ground straw by calculating the displaced volume of nitrogen gas by a known mass of material, following the method reported by Adapa et al. (2005). Three replicates for each sample were performed for both bulk and particle density measurements.

5.4.6 Chemical Composition and Higher Heating Values

The chemical composition analysis of non-treated and steam exploded barley, canola, oat and wheat straw was performed in duplicates by the SunWest Food Laboratory Ltd., Saskatoon, SK, Canada, and the Feed Innovation Centre, University of Saskatchewan, respectively. Crude protein, crude fat, starch, lignin, acid detergent fibre (ADF), neutral detergent fibre (NDF) and total ash contents were determined using standard methods. The crude protein content of the biomass was determined using the AOAC standard method 2001.11 (AOAC, 2001), where the nitrogen content was multiplied by a factor 6.25. The crude fat was determined using AOCS standard method Am2-93 (AOCS, 1999). Total starch content was measured using AOAC standard method 996.11 (AOAC, 1998). The lignin and ADF were determined using AOAC standard method 973.18 (AOAC, 1990a), whereas NDF was determined using AOAC standard method 992.16 (AOAC, 1990b). The total ash content was determined using AOAC standard method 942.05 (AOAC, 1990c). The cellulose percentage was calculated indirectly from percentage acid detergent fibre (ADF) and lignin (%ADF minus %lignin) (Mani et al., 2006b). Hemicellulose percentage was calculated indirectly from percentage neutral detergent fibre (NDF) and ADF (% NDF minus %ADF) (Mani et al., 2006b).

The calorific (heating) value of biomass feedstocks are indicative of the energy they possess as potential fuels. The gross calorific value (higher heating value, HHV) and the net calorific value (lower heating value, LHV) at constant pressure measures the enthalpy change of combustion with and without water condensed, respectively (Demirbaş, 2007). A Parr 1281 automatic isoperibol oxygen bomb calorimeter (Parr Instrument Company, Moline, IL) was used to determine the HHV of the non-treated and steam exploded straw in MJ/kg at the Feed Innovation Centre, University of Saskatchewan. ASTM Standard D5865-03 (ASTM, 2003) test method for gross calorific value of coal and coke, was used as a guideline for heating value testing.

5.4.7 Experimental Set-up

A compaction apparatus having a close fit plunger die assembly (Adapa et al., 2006) was used to study the compression characteristics of selected agricultural straw (Adapa et al., 2002). The cylindrical die was 135.3 mm long and 6.30±0.5 mm in diameter. A thermal compound (Wakefield Engineering Inc., Wakefield, MA) was coated on the outer surface of the die prior to

wrapping the outer surface with copper shim stock. A dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, IL) was then wound evenly around the shim stock to provide the necessary heat. One type-T thermocouple, connected to the outer surface of the cylinder, was linked to a temperature controller to regulate the power input to the heater, thus allowing temperature control of the cylinder. Another type-T thermocouple was also connected to the outer cylinder wall, allowed verification of the cylinder temperature via a digital thermocouple reader (Shaw 2008). The die was fitted on a stainless steel base having a hole matching its outer diameter. This gave stability and allowed the plunger to move straight down with no lateral movement. The plunger was attached to the upper moving crosshead of the Instron Model 1011 testing machine (Instron Corp., Canton, MA).

5.4.8 Compression Test and Energy Calculations

Prior to the compression experiments, the biomass was re-moistened to 10% moisture content (wb) by adding/sprinkling a calculated amount of water on the sample and mixed thoroughly. The samples were subsequently stored in plastic bags and kept in a cold room at 4^{o}C for a minimum of 72 h. Only one moisture level of 10% (wb) was used based upon literature review, which reiterated that at this moisture level, high density and quality pellets/briquettes were produced from various straw and biomass (Kaliyan and Morey, 2006a and 2007; Mani et al., 2006b; Obernberger and Thek, 2004; Shaw and Tabil, 2007; Stevens, 1987).

The compaction apparatus was used to make a single compact in one stroke of the plunger from ground straw samples. In order to simulate frictional heating during commercial pelleting operation, the compaction die was maintained at a temperature of 95±1^{o}C (Adapa et al., 2006 and Mani et al., 2006b). The mass of samples used for making compacts varied between 0.5 and 0.7 g. Compressive force was applied using the Instron Model 1011 testing machine fitted with a 5000 N load cell and a 6.25 mm diameter plunger. Four preset loads of 1000, 2000, 3000 and 4400 N corresponding to pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were used to compress samples in the die. The crosshead speed of the Instron testing machine was set at 50 mm/min. After compression, the plunger was retained in place for 30 s once the preset load was attained in order to avoid spring-back effect of biomass grinds (Adapa et al., 2006 and Mani et al., 2006b). Later, the base plate was removed and the compact was ejected out of the die by using the plunger. The mass, length and diameter of compacts were measured to determine the density in

kg/m^3, following the extrusion of the compact. Ten replicates (pellets) were made using each ground straw samples.

During compression and extrusion process of individual compacts, the force-displacement data were recorded. Specific compression and extrusion energies were calculated following the methodology of Mani et al. (2006a). The area under the force-displacement curve was integrated using the trapezoid rule (Cheney and Kincaid, 1980); when combined with the pellet mass, it yielded the specific energy values in MJ/t. The specific energy calculations did not include the energy required to operate the Instron testing machine.

In this study, the compacts were prepared by densifying material against a base plate (representing the specific energy required to overcome friction within the straw grinds) as opposed to commercial operation where pellets are formed due to back-pressure effect in the die. However, the specific energy required to extrude the compact was included, which will closely emulate the specific energy required to overcome the friction between the ground straw and die.

5.4.9 Statistical Analysis

The experiments were set up as completely randomized experimental design with 10 replications of compacts and four-variable (straw, pre-treatment (steam explosion), hammer mill screen size and pressure) factorial design. Density was the dependent variable, while straw, pre-treatment, hammer mill screen size and pressure were the independent variables. Statistical analyses were conducted using SAS for Windows (version 8.2) (SAS Institute, 1999). In order to further understand and explain the experimental variables and their interactions, the SAS general linear model (GLM) for completely randomized design (CRD) procedure was used and the Student-Neuman-Keuls test (SNK) was performed. SNK determines the difference between any two treatment means at 5% level of significance (SAS Manual, SAS Institute, 1999).

5.5 Results and Discussion

5.5.1 Properties of the Ground Biomass

The geometric mean particle diameter, bulk density and particle density of ground barley, canola, oat and wheat straws are shown in Table 5.1.

Geometric Mean Particle Diameter: In general, for non-treated and steam exploded biomass grinds, the geometric mean particle diameter significantly decreased with a decrease in hammer mill screen sizes of 6.4, 3.2 and 1.6 mm having a few exceptions (Table 5.1). At any specific hammer mill screen size, the mean particle diameters of non-treated biomass were significantly different at 3.2 and 1.6 mm screen sizes. However, the geometric mean diameter for different steam exploded biomass was not significantly different from each other, except for canola and wheat (0.387±0.005 mm) at 3.2 mm and canola at 1.6 mm hammer mill screen sizes. This could be due to the fact that steam explosion disintegrates the natural cellulose-hemicellulose-lignin matrix thus resulting in similar structural properties.

The geometric mean particle diameter of steam exploded straw at any specific hammer mill screen size was significantly lower than non-treated straw.

Bulk Density: The bulk density of ground non-treated and steam exploded barley, canola, oat and wheat straw significantly increased with a decrease in hammer mill screen sizes (Table 5.1). Similar to the geometric mean particle diameter, at any specific hammer mill screen size, the bulk densities of non-treated biomass were significantly different. However, the bulk densities for different steam exploded biomass were not significantly different from each other, having a few exceptions.

The bulk density of non-treated barley, canola, oat and wheat straw grinds at any specific hammer mill screen size was significantly higher than steam exploded straw (Table 5.1) indicating that steam explosion pretreatment disintegrates the organized and compact lignocellulosic structure of biomass resulting in lower bulk densities.

Particle Density: The particle density of non-treated and steam exploded barley, canola, oat and wheat straws significantly increased with a decrease in hammer mill screen sizes, except for barley and wheat straw at 3.2 and 1.6 mm hammer mill screen sizes (Table 5.1).

Similar to the geometric mean particle diameter and bulk density, at any specific hammer mill screen size, the particle densities of non-treated biomass were significantly different. However, the particle densities for different steam exploded biomass were not significantly different from each other, having a few exceptions.

In general, the particle density of steam exploded barley, canola, oat and wheat straw at any specific hammer mill screen size was significantly higher than non-treated straw. This could be due to application of steam explosion pretreatment which disintegrated the long chain lignocellulosic structure into short chains leading to higher particle densities.

Table 5.1: Moisture content, geometric mean particle size, bulk and particles densities for non-treated and steam exploded barley, canola, oat and wheat straw samples.

Agricultural Biomass	Hammer Mill Screen Size (mm)	Moisture Content Post-Grinding (%, wb)	Geometric Mean Particle Diameter (mm)	Bulk Density (kg/m^3)	Particle Density (kg/m^3)
Non-Treated Straw					
Barley Straw	6.4	8.9±0.4[‡†]	0.883±0.025 aDX[£]	96±02 aDX	1016±137 aDEX
	3.2	5.3±0.3	0.463±0.016 bDX	149±03 bDEX	1089±32 aDX
	1.6	7.8±0.2	0.456±0.004 bDX	155±01 cDX	1149±02 aDX
Canola Straw	6.4	12.6±0.2	0.885±0.020 aDX	144±02 aEX	1019±19 aDEX
	3.2	9.2±0.1	0.521±0.061 bDEX	190±09 bFX	1192±11 bEX
	1.6	8.3±0.2	0.367±0.001 cEX	203±11 bEX	1309±02 cEX
Oat Straw	6.4	10.9±0.1	0.935±0.013 aDX	111±08 aFX	873±18 aEX
	3.2	9.4±0.3	0.566±0.015 bEX	156±04 bDX	1093±38 bDX
	1.6	7.7±0.1	0.404±0.014 bFX	196±04 cEX	1240±18 cFX
Wheat Straw	6.4	9.5±0.4	0.997±0.038 aEX	107±02 aFX	1078±14 aDX
	3.2	9.5±0.3	0.719±0.015 bFX	141±02 bEX	1225±11 bEX
	1.6	8.6±0.3	0.452±0.016 cDX	154±02 cDX	1269±23 bDX
Steam Exploded Straw					
Barley Straw	6.4	5.8±0.3	0.607±0.028 aDY	38±03 aDY	1033±19 aDX
	3.2	4.8±0.2	0.368±0.002 bDY	73±02 bDY	1342±60 bDY
	1.6	4.6±1.2	0.296±0.013 cDY	93±06 cDY	1415±79 bDY

Canola Straw	6.4	4.3±0.0	0.698±0.127 aDY	33±02 aEY	968±38 aDX
	3.2	4.2±0.1	0.447±0.010 bEY	44±00 bEY	1138±17 bEY
	1.6	4.6±0.1	0.364±0.007 bEY	67±02 cEY	1294±17 cDX
Oat Straw	6.4	4.6±0.2	0.602±0.012 aDY	43±01 aFY	1143±23 aEY
	3.2	4.5±0.1	0.367±0.010 bDY	77±04 bDY	1272±13 bDY
	1.6	4.1±0.2	0.327±0.022 cDY	91±03 cDY	1368±18 cDY
Wheat Straw	6.4	4.5±0.2	0.568±0.10 aDY	41±01 aDFY	1119±52 aEX
	3.2	4.7±0.4	0.387±0.005 bFY	73±05 bDY	1314±32 bDY
	1.6	4.3±0.3	0.309±0.012 cDY	100±05 cDY	1380±80 bDX

‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass at various hammer mill screen sizes (a, b and c); at same hammer mill screen size for different sample biomass (D, E and F); for any particular biomass at same hammer mill screen size for non-treated and steam exploded biomass (X and Y)

5.5.2 Chemical Composition and Higher Heating Values (HHV)

Table 5.2 enumerates the average chemical composition of non-treated and steam exploded barley, canola, oat and wheat straw samples for tests performed in duplicates. The non-treated canola straw has the highest protein content (6.53%); barley straw has the highest level of fat (1.91%) and lignin (17.13%), while wheat straw showed the highest levels of starch (2.58%) and ash (2.36%) contents. The steam exploded canola straw has the highest protein content (2.21%), canola straw has the highest level of lignin content (12.04%), barley straw has the highest level of starch content (0.38%) and ash content (3.62%). Non-treated canola and wheat straw showed highest level of cellulose (42.39%) and hemicelluloses content (23.68%), respectively, while steam exploded oat and barley straw showed highest level of cellulose (47.52%) and hemicelluloses (26.49%), respectively.

Cellulose, hemicelluloses and lignin are major components of a plant biomass. Therefore, a change in their composition could potentially lead to change in HHV of the biomass. The cellulose content of steam exploded barley, canola, oat and wheat straw was 37%, 7%, 26% and 36% higher than non-treated straw, respectively. The hemicelluloses content of steam exploded barley, canola and oat straw was 30%, 6% and 9% higher; however wheat straw was 14% lower than non-treated straw, respectively. The lignin content of steam exploded barley, canola, oat and wheat straw was 50%, 15%, 25% and 14% lower than non-treated straw, respectively. These observations were contrary to Shaw (2008) where a decrease in cellulose and

hemicelluloses content and an increase in lignin content of steam exploded poplar wood and wheat straw were reported. This could be due to the fact that they have performed the steam explosion at 200-205^{o}C (steam pressure of 1.66 to 1.73 MPa) for 4-5.5 min as opposed to the present study in which steam explosion was performed at 180^{o}C for 4 min.

Net combined percentage change of cellulose, hemicelluloses and lignin in steam exploded barley, canola, oat and wheat straw is 17%, -2%, 10% and 8% higher than non-treated straw, respectively. As a result, the average HHV of steam exploded barley, canola, oat and wheat straw was 6%, 10%, 9% and 5% higher than non-treated straw, respectively (Table 5.2). An increase in HHV for steam exploded canola straw could be due to a 4% decrease in ash content. Similar observations of increase in HHV with a decrease in ash content was reported by Shaw (2008) and Sheng and Azevedo (2005).

Table 5.2: Chemical composition and higher heating values of non-treated and steam exploded barley, canola, oat and wheat straw

Properties of Biomass	Barley Straw		Canola Straw		Oat Straw		Wheat Straw	
	NT	SE	NT	SE	NT	SE	NT	SE
Composition (% of dry matter)								
Protein	3.62	1.49	6.53	2.21	5.34	1.19	2.33	1.08
Fat	1.91	ND	0.69	ND	1.65	ND	1.59	ND
Starch	0.11	0.38	0.34	0.18	0.12	0.22	2.58	0.30
Lignin	17.13	8.64	14.15	12.04	12.85	9.64	13.88	11.89
Cellulose[a]	33.25	45.48	42.39	45.29	37.60	47.52	34.20	46.64
Hemicellulose[b]	20.36	26.49	16.41	17.36	23.34	25.33	23.68	20.39
Ash	2.18	3.62	2.10	2.02	2.19	3.47	2.36	3.30
Higher Heating Values (MJ/kg of dry matter)								
HHV (MJ/kg)	16.4±0.3‡†	17.4±0.1	16.7±0.3	18.3±0.0	16.4±0.1	17.8±0.0	17.0±0.2	17.8±0.0

NT – Non-treated; SE – Steam Exploded agricultural biomass; ND – Not Determined

[a]Cellulose percentage is calculated indirectly from percentage acid detergent fiber (ADF) and lignin (%ADF-%lignin) (Mani et al., 2006b).

[b]Hemicellulose percentage is calculated indirectly from percentage neutral detergent fiber (NDF) and ADF (%NDF-%ADF) (Mani et al., 2006b)

HHV – Higher Heating Values (Parr 1281 Bomb Calorimeter)

‡3 replicates; † 95% confidence interval

5.5.3 Compact Density

Tables 5.3, 5.4, 5.5 and 5.6 show the effect of applied pressure on compact density made from ground non-treated and steam exploded barley, canola, oat and wheat straw, respectively. Figures 5.2 and 5.3 depict the photographs of compacts made from ground non-treated and steam exploded straw, respectively. For non-treated straw, a visual inspection of the pellets shows that the surface of pellet appears to be smooth and shiny, and appear to have higher density with a decrease in hammer mill grind size (Figure 5.2). Pellets from steam exploded straw appear to have higher density as compared to non-treated straw (Figures 5.2 and 5.3). For non-treated and steam exploded barley, canola, oat and wheat straw at any particular hammer mill screen size, the compact density significantly increased with an increase in applied pressure, with a few exceptions.

At any given pressure, the compact density of non-treated barley straw was not statistically different for different hammer mill screen sizes. However, for steam exploded barley straw at any given pressure, the compact density was not statistically different for 3.2 and 1.6 mm screen sizes, except at a pressure of 63.2 MPa. The compact density of steam exploded barley straw obtained at any pressure for 6.4 mm screen size was significantly lower than 3.2 and 1.6 mm screen sizes, except at 94.7 MPa (Table 5.3). The compact density of steam exploded barley straw was significantly higher than non-treated straw for all hammer mill screen sizes and pressures.

The compact density of non-treated canola straw was not statistically different for 3.2 and 1.6 mm screen sizes, at any particular pressure. However, the compact density at 6.4 mm screen size was significantly lower than 3.2 and 1.6 mm, except at 31.6 MPa, and 94.7 MPa for 3.2 mm screen size only (Table 5.4). For steam exploded canola straw at any particular pressure, the compact density was not statistically different for 6.4, 3.2 and 1.6 mm, except for 1.6 mm screen size at 31.6 MPa, and 3.2 mm and 1.6 mm screen at 63.2 MPa (Table 5.4). The compact density of steam exploded canola straw was significantly higher than non-treated straw for all hammer mill screen sizes and pressures.

The compact density obtained for non-treated oat straw at any particular pressure was not statistically different for three selected screen sizes, except for 3.2 and 1.6 mm screen size at 63.2

MPa, and 3.2 mm screen size at 94.7 MPa (Table 5.5). Similarly, the compact density of steam exploded oat straw at any particular pressure was not statistically different for various screen sizes, except for 3.2 and 1.6 mm screen sizes at 31.6 and 63.2 MPa (Table 5.5). The compact density of steam exploded oat straw was significantly higher than non-treated straw for all hammer mill screen sizes and pressures.

The compact density of non-treated wheat straw at any particular pressure for various screen sizes was not statistically different, except for 1.6 mm screen size at pressures of 31.6 and 63.2 MPa (Table 5.6). Similarly, the compact density of steam exploded wheat straw at any particular pressure for various screen sizes was not statistically different, except for 1.6 mm screen size at 63.2 MPa (Table 5.6). The compact density of steam exploded wheat straw was significantly higher than non-treated straw for all hammer mill screen sizes and pressures.

The compact density of steam exploded barley, canola, oat and wheat straw was significantly higher than non-treated straw for all hammer mill screen sizes and pressures (Tables 5.3-5.6), which corresponds to lower geometric mean particle diameters and higher particle densities of steam exploded straw (Table 5.1). It was also postulated that during the steam explosion process, the hemicelluloses are hydrolyzed and become water soluble, the cellulose is slightly depolymerized, and the lignin melts and is depolymerized resulting in better compacts as compared to non-treated straw (Shaw, 2008; Toussaint et al., 1991). In general, it can be concluded that for non-treated and steam exploded barley, canola, oat and wheat straw, pressure and pre-treatment are significant factors effecting the compact density. In addition, ground steam exploded barley straw at screen sizes of either 3.2 or 1.6 mm produced high density compacts, while ground steam exploded canola, oat and wheat straw at screen sizes of 6.4, 3.2 or 1.6 mm produced high density compacts.

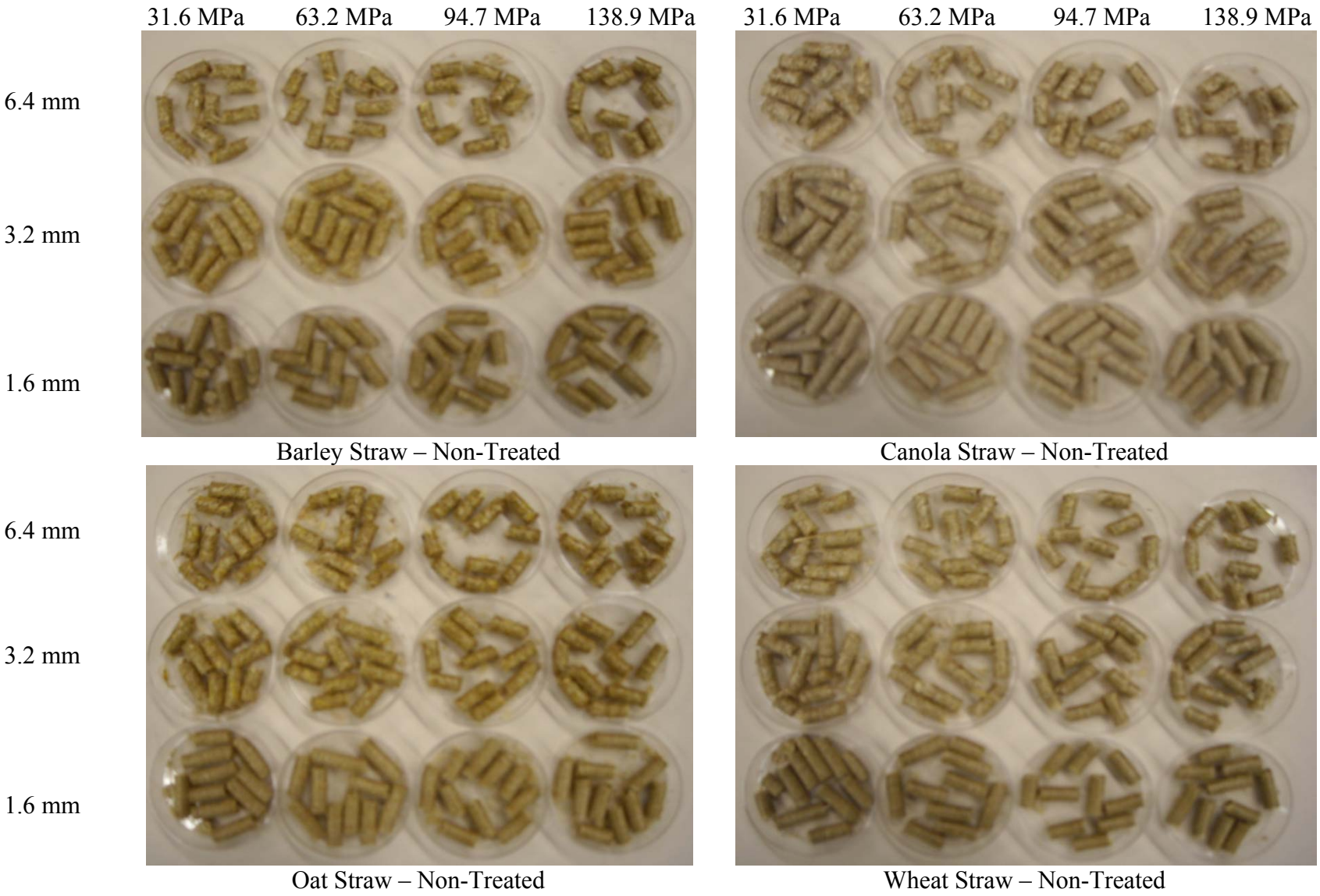


Figure 5.2: Photograph of compacts made from ground non-treated barley, canola, oat and wheat straw

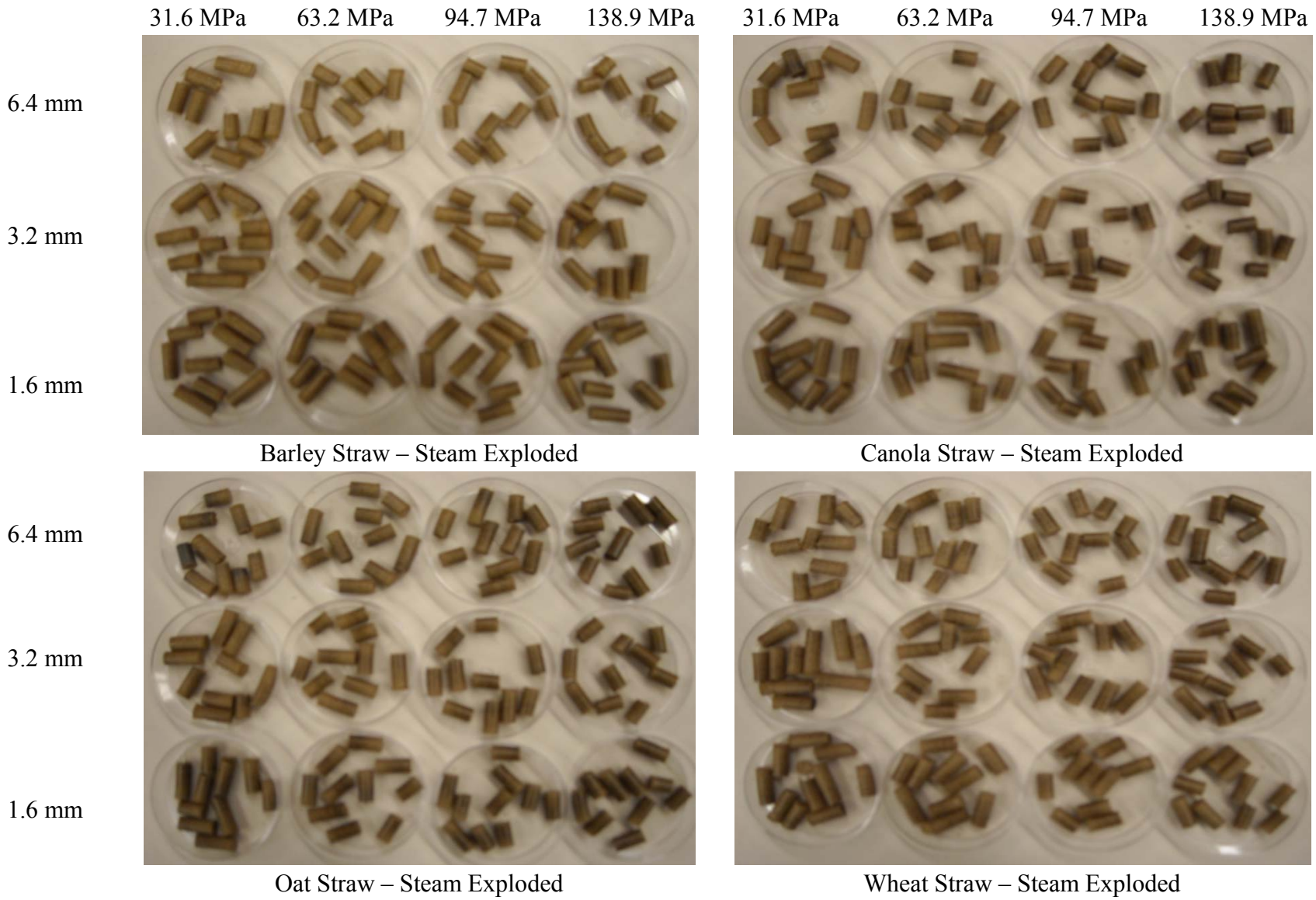


Figure 5.3: Photograph of compacts made from ground non-treated barley, canola, oat and wheat straw.

Table 5.3: Measured pellet mass, diameter and length; and calculated volume and density data for non-treated and steam exploded barley straw at 10% moisture content (wb).

Barley Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Compact Mass (g)	Compact Diameter (mm)	Compact Length (mm)	Volume (mm^3)		Compact Density (kg/m^3)	Specific Energy (MJ/t)	
						V	Vs		Compression	Total[¥]
Non-Treated	6.4	1000 / 31.6	0.386±0.023[‡†]	6.63±0.02	14.01±0.92	483±30	380±23	798±19 aDX[£]	7.12±0.86 aDX	7.31±0.90 aDX
		2000 / 63.2	0.398±0.029	6.62±0.04	12.41±0.91	426±31	392±28	934±40 bDX	10.08±2.00 bDX	10.37±2.19 bDX
		3000 / 94.7	0.397±0.035	6.60±0.02	11.70±1.06	401±37	391±35	991±24 cDX	13.40±1.00 cDX	14.07±1.18 cDX
		4400 / 138.9	0.415±0.025	6.61±0.02	12.06±0.78	414±27	408±24	1003±32 cDX	14.61±0.97 dDX	15.25±1.09 cDX
	3.2	1000 / 31.6	0.496±0.049	6.57±0.04	18.56±2.09	630±77	455±45	788±27 aDX	8.14±0.72 aEX	8.96±0.79 aEX
		2000 / 63.2	0.550±0.085	6.60±0.02	17.52±2.43	600±85	505±78	915±28 bDX	11.72±1.07 bEX	13.00±1.15 bEX
		3000 / 94.7	0.518±0.028	6.60±0.03	15.50±0.87	531±32	476±26	976±18 cDX	12.66±1.01 cDX	14.09±1.15 cDX
		4400 / 138.9	0.570±0.039	6.62±0.03	16.15±0.94	556±35	523±35	1024±25 dDX	14.90±0.80 dDX	16.37±1.06 dEX
	1.6	1000 / 31.6	0.447±0.088	6.54±0.04	17.06±3.32	574±114	389±76	781±38 aDX	5.68±0.70 aFX	6.03±0.83 aFX
		2000 / 63.2	0.476±0.029	6.56±0.03	15.44±1.13	522±38	415±25	914±19 bDX	8.16±0.41 bFX	8.80±0.51 bFX
		3000 / 94.7	0.496±0.038	6.56±0.01	15.11±1.07	510±37	432±33	972±12 cDX	9.83±0.45cEX	10.59±0.51 cEX
		4400 / 138.9	0.542±0.042	6.58±0.02	16.04±0.92	545±31	472±36	994±28 cDX	12.22±0.34 dEX	13.10±0.40 dFX
Steam Exploded	6.4	1000 / 31.6	0.380±0.048	6.51±0.03	12.69±1.70	422±56	368±46	903±43 aDY	7.60±0.47 aDX	7.80±0.49 aDX
		2000 / 63.2	0.387±0.069	6.49±0.01	10.87±2.05	359±68	375±67	1081±24 bDY	9.98±0.54 bDX	10.13±0.53 bDX
		3000 / 94.7	0.387±0.041	6.51±0.02	10.31±1.16	343±38	375±39	1131±25 cDY	12.31±0.33 cDY	12.43±0.31 cDY
		4400 / 138.9	0.302±0.047	6.52±0.02	8.09±1.03	270±33	293±45	1116±62 bcDY	15.75±1.23 dDY	15.89±1.25 dDX
	3.2	1000 / 31.6	0.409±0.091	6.51±0.03	13.90±2.93	463±98	304±68	882±32 aEY	5.95±0.45 aEY	6.30±0.57 aEY
		2000 / 63.2	0.441±0.074	6.51±0.02	13.00±2.36	432±78	328±55	1022±28 bEY	9.05±0.77 bEY	9.21±0.76 bEY
		3000 / 94.7	0.459±0.077	6.51±0.02	12.18±2.00	406±67	342±58	1130±22 cDY	10.09±0.68 cEY	10.22±0.71 cEY
		4400 / 138.9	0.510±0.087	6.50±0.02	13.22±2.09	439±69	380±65	1159±35 dEY	13.13±0.42 dEY	13.31±0.40 dEY
	1.6	1000 / 31.6	0.492±0.071	6.49±0.02	16.00±2.56	529±83	347±50	931±21 aDEY	5.78±0.71 aEX	6.00±0.75 aEX
		2000 / 63.2	0.516±0.060	6.48±0.01	14.85±1.74	490±57	365±42	1053±18 bFY	7.77±0.37 bFY	7.90±0.39 bFY
		3000 / 94.7	0.535±0.059	6.49±0.02	14.55±1.61	481±54	378±42	1112±23 cDY	9.95±0.44 cEX	10.09±0.44 cEY
		4400 / 138.9	0.562±0.069	6.49±0.02	14.54±1.70	481±56	397±49	1169±12 dEY	12.43±0.45 dEX	12.59±0.43 dEY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); V - Compact volume; Vs – Void free compact volume; ¥ Total Specific Energy = Specific Energy for Compression + Specific Energy for Extrusion.

Table 5.4: Measured pellet mass, diameter and length; and calculated volume and density data for non-treated and steam exploded canola straw at 10% moisture content (wb).

Canola Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Compact Mass (g)	Compact Diameter (mm)	Compact Length (mm)	Volume (mm^3)		Compact Density (kg/m^3)	Specific Energy (MJ/t)	
						V	Vs		Compression	Total[¥]
Non-Treated	6.4	1000 / 31.6	0.407±0.059[‡†]	6.63±0.03	14.87±2.34	513±82	399±60	795±38 aDX[£]	13.03±1.57 aDX	13.77±1.69 aDX
		2000 / 63.2	0.417±0.050	6.60±0.02	12.51±1.45	428±51	409±47	974±29 bDX	14.85±1.90 aDX	15.59±2.03 aDX
		3000 / 94.7	0.513±0.050	6.61±0.01	14.79±1.24	507±42	502±48	1009±35 bDX	17.87±1.96 bDX	19.10±2.15 bDX
		4400 / 138.9	0.474±0.067	6.61±0.03	13.90±1.75	478±61	465±67	990±38 bDX	18.34±2.57 bDX	19.46±2.90 bDX
	3.2	1000 / 31.6	0.507±0.028	6.59±0.02	19.11±1.09	651±37	425±22	779±22 aDX	7.60±0.71 aEX	8.22±0.72 aEX
		2000 / 63.2	0.544±0.049	6.60±0.01	17.10±1.60	585±55	457±41	933±42 bEX	10.16±0.61 bEX	10.92±0.66 bEX
		3000 / 94.7	0.578±0.053	6.61±0.02	16.98±1.58	583±56	486±45	994±21 cDEX	12.37±0.61 cEX	13.17±0.75 cEX
		4400 / 138.9	0.559±0.061	6.59±0.02	15.79±1.48	538±53	468±49	1035±18 dEX	13.75±0.42 dEX	14.63±0.52 dEX
	1.6	1000 / 31.6	0.566±0.042	6.56±0.03	21.30±2.06	719±73	433±32	791±30 aDX	5.31±0.30 aFX	5.67±0.30 aFX
		2000 / 63.2	0.614±0.054	6.56±0.02	19.81±1.48	670±53	467±40	912±19 bEX	8.30±0.56 bFX	8.90±0.47 bFX
		3000 / 94.7	0.629±0.043	6.61±0.03	18.79±1.34	644±48	480±32	976±16 cEX	10.16±0.69 cFX	10.93±0.71 cFX
		4400 / 138.9	0.655±0.025	6.60±0.02	18.59±0.79	636±27	499±20	1027±22 dEX	12.65±0.25 dEX	13.59±0.26 dEX
Steam Exploded	6.4	1000 / 31.6	0.307±0.055	6.57±0.02	10.71±2.02	363±70	317±56	849±47 aDY	7.20±1.22 aDY	9.29±2.15 aDY
		2000 / 63.2	0.357±0.073	6.56±0.02	10.35±1.85	350±63	369±76	1016±35 bDY	10.96±0.93 bDY	13.45±1.09 bDY
		3000 / 94.7	0.419±0.036	6.56±0.01	11.25±1.05	380±36	433±37	1105±27 cDY	14.81±1.39 cDY	20.44±2.58 cDX
		4400 / 138.9	0.410±0.036	6.56±0.01	10.52±0.88	355±30	423±37	1154±27 dDY	18.22±1.03 dDX	23.08±1.21 dDY
	3.2	1000 / 31.6	0.385±0.056	6.57±0.02	13.38±1.46	453±48	338±49	846±41aDY	9.31±0.68 aEY	12.90±1.16 aEY
		2000 / 63.2	0.387±0.048	6.55±0.01	10.86±1.33	366±45	340±42	1059±25 bEY	11.13±0.55 bDY	14.32±0.86 aDY
		3000 / 94.7	0.405±0.044	6.55±0.02	10.69±1.26	360±44	356±39	1126±33 cDY	13.81±1.69 cDY	18.28±3.32 bDY
		4400 / 138.9	0.417±0.048	6.54±0.01	10.66±1.30	358±44	366±42	1165±26 dDY	16.12±0.61 dEY	20.53±1.27 cEY
	1.6	1000 / 31.6	0.457±0.042	6.57±0.02	14.63±1.20	496±42	353±32	923±31 aEY	7.09±0.57 aDY	9.89±0.84 aDY
		2000 / 63.2	0.479±0.070	6.56±0.01	13.27±2.05	448±70	370±54	1070±20 bEY	9.59±0.91 bEY	12.29±1.39 bEY
		3000 / 94.7	0.443±0.079	6.54±0.01	11.73±1.93	394±66	343±61	1123±16 cDY	11.90±0.76 cEY	14.20±0.95 cEY
		4400 / 138.9	0.493±0.072	6.55±0.01	12.59±1.70	424±58	381±56	1163±24 dDY	13.93±0.81 dFY	16.58±1.50 dFY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); V - Compact volume; Vs – Void free compact volume; ¥ Total Specific Energy = Specific Energy for Compression + Specific Energy for Extrusion.

Table 5.5: Measured pellet mass, diameter and length; and calculated volume and density data for non-treated and steam exploded oat straw at 10% moisture content (wb).

Oat Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Compact Mass (g)	Compact Diameter (mm)	Compact Length (mm)	Volume (mm^3)		Compact Density (kg/m^3)	Specific Energy (MJ/t)	
						V	Vs		Compression	Total[¥]
Non-Treated	6.4	1000 / 31.6	0.423±0.042[‡†]	6.68±0.03	14.81±1.78	519±62	484±48	817±26 aDX[£]	9.72±1.05 aDX	10.24±1.19 aDX
		2000 / 63.2	0.433±0.047	6.63±0.04	13.28±1.53	458±55	495±54	945±24 bDX	13.65±2.68 bDX	14.52±2.88 bDX
		3000 / 94.7	0.457±0.067	6.61±0.03	13.50±1.71	464±61	523±77	982±29 cDX	13.73±1.74 bDX	14.59±1.70 bDX
		4400 / 138.9	0.419±0.042	6.64±0.03	12.27±0.91	424±31	479±49	985±43 cDX	16.41±2.21 cDX	17.27±2.23 cDX
	3.2	1000 / 31.6	0.440±0.042	6.60±0.05	15.88±1.69	543±60	402±39	811±26 aDX	7.92±0.71 aEX	8.74±0.70 aEX
		2000 / 63.2	0.493±0.062	6.62±0.04	15.80±1.88	544±66	451±57	907±24 bEX	9.78±0.63 bEX	10.74±0.71 bEX
		3000 / 94.7	0.477±0.052	6.62±0.02	14.59±1.35	502±48	436±47	948±24 cEX	12.15±1.27 cEX	13.24±1.55 cEX
		4400 / 138.9	0.498±0.061	6.62±0.04	14.62±1.71	504±61	455±56	988±35 dDX	14.68±0.97 dEX	15.94±0.99 dDX
	1.6	1000 / 31.6	0.503±0.050	6.53±0.04	18.92±2.27	633±77	405±40	795±23 aDX	5.85±0.46 aFX	6.56±0.53 aFX
		2000 / 63.2	0.584±0.056	6.57±0.01	18.90±1.83	641±63	471±45	912±17 bEX	8.47±0.56 bEX	9.51±0.75 bEX
		3000 / 94.7	0.539±0.065	6.56±0.02	16.11±2.04	544±72	435±53	992±26 cDX	10.13±0.81 cFX	11.46±1.04 cFX
		4400 / 138.9	0.567±0.045	6.57±0.03	16.33±1.20	553±42	457±36	1024±26 dDX	11.99±0.56 dFX	13.26±0.82 dEX
Steam Exploded	6.4	1000 / 31.6	0.369±0.046	6.58±0.02	12.20±1.53	415±54	323±40	889±30 aDY	8.22±1.07 aDY	12.12±1.91 aDY
		2000 / 63.2	0.454±0.073	6.58±0.02	12.90±1.83	439±64	397±64	1034±55 bDY	13.17±1.58 bDX	18.57±2.37 bDY
		3000 / 94.7	0.490±0.082	6.56±0.02	12.80±2.04	433±68	429±72	1130±32 cDY	15.77±1.69 cDY	19.95±2.57 bDY
		4400 / 138.9	0.489±0.077	6.55±0.01	12.58±1.81	424±61	428±68	1151±21 cDY	14.66±1.27 cDY	17.84±1.57 bDX
	3.2	1000 / 31.6	0.458±0.069	6.58±0.02	14.61±2.19	497±76	360±54	923±40 aEY	8.41±0.72 aDX	11.09±0.97 aDEY
		2000 / 63.2	0.465±0.085	6.56±0.01	12.92±2.51	437±85	366±67	1068±17 bEY	10.42±1.00 bEX	12.93±1.41 bEY
		3000 / 94.7	0.474±0.061	6.56±0.01	12.44±1.51	420±52	373±48	1129±30 cDY	12.59±0.89 cEX	14.96±1.13 cEY
		4400 / 138.9	0.426±0.075	6.55±0.01	11.07±2.00	373±68	335±59	1144±14 cDY	14.97±0.64 dDX	17.85±1.62 dDY
	1.6	1000 / 31.6	0.466±0.078	6.56±0.02	14.44±2.31	488±79	341±57	954±20 aFY	7.47±0.79 aDY	9.84±1.16 aEY
		2000 / 63.2	0.490±0.051	6.55±0.02	13.33±1.38	450±47	358±37	1090±16 bEY	10.42±0.85 bEY	12.44±0.74 bEY
		3000 / 94.7	0.463±0.067	6.55±0.01	12.03±1.68	405±56	338±48	1143±16 cDY	11.83±0.58 cEY	13.84±0.51 cEY
		4400 / 138.9	0.478±0.068	6.55±0.01	12.18±1.66	410±57	349±49	1165±27 dDY	14.29±0.89 dDY	16.88±1.16 dDY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); V - Compact volume; Vs – Void free compact volume; ¥ Total Specific Energy = Specific Energy for Compression + Specific Energy for Extrusion.

Table 5.6: Measured pellet mass, diameter and length; and calculated volume and density data for non-treated and steam exploded wheat straw at 10% moisture content (wb).

Wheat Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Compact Mass (g)	Compact Diameter (mm)	Compact Length (mm)	Volume (mm^3)		Compact Density (kg/m^3)	Specific Energy (MJ/t)	
						V	Vs		Compression	Total[¥]
Non-Treated	6.4	1000 / 31.6	0.398±0.054[‡†]	6.61±0.04	14.83±2.20	510±79	369±50	782±22 aDX[£]	10.95±1.66 aDX	11.54±1.84 aDX
		2000 / 63.2	0.430±0.032	6.60±0.03	13.60±0.80	466±29	399±30	923±32 bDX	12.78±0.77 bDX	13.42±0.79 bDX
		3000 / 94.7	0.399±0.027	6.60±0.02	12.09±0.85	414±30	370±25	965±52 cDX	13.90±1.80 bDX	14.48±1.94 bDX
		4400 / 138.9	0.420±0.018	6.59±0.03	12.30±0.70	420±22	390±17	1001±21 dDX	16.89±1.19 cDX	17.56±1.30 cDX
	3.2	1000 / 31.6	0.448±0.068	6.55±0.04	17.09±2.71	576±91	365±56	778±22 aDX	6.61±0.52 aEX	7.00±0.55 aEX
		2000 / 63.2	0.476±0.031	6.57±0.02	15.32±1.02	519±35	389±26	917±17 bDX	9.32±0.53 bEX	9.79±0.56 bEX
		3000 / 94.7	0.498±0.055	6.56±0.03	15.23±1.68	516±58	407±45	967±27 cDX	10.24±0.44 cEX	10.82±0.48 cEX
		4400 / 138.9	0.490±0.057	6.55±0.04	14.42±1.53	486±53	400±47	1007±26 dDX	12.44±1.18 dEX	13.08±1.24 dEX
	1.6	1000 / 31.6	0.502±0.057	6.55±0.02	18.22±2.03	614±69	396±45	819±23 aEX	5.09±0.39 aFX	5.46±0.41 aFX
		2000 / 63.2	0.569±0.067	6.56±0.02	17.77±2.09	600±72	448±53	948±18 bEX	7.58±0.38 bFX	8.08±0.42 bFX
		3000 / 94.7	0.503±0.036	6.56±0.02	14.91±0.85	504±30	396±28	997±19 cDX	8.88±0.36 cFX	9.48±0.41 cFX
		4400 / 138.9	0.545±0.073	6.58±0.02	15.88±1.97	540±67	429±57	1009±21 cDX	11.24±0.30 dFX	11.96±0.32 dFX
Steam Exploded	6.4	1000 / 31.6	0.346±0.044	6.56±0.01	11.50±1.61	388±55	309±40	893±39 aDY	9.01±0.89 aDY	11.44±1.43 aDX
		2000 / 63.2	0.413±0.047	6.54±0.01	11.50±1.36	389±47	369±42	1064±26 bDEY	11.93±0.77 bDY	14.71±1.01 bDY
		3000 / 94.7	0.403±0.054	6.55±0.01	10.71±1.45	361±50	360±48	1118±23 cDY	14.83±1.06 cDX	17.66±2.07 cDY
		4400 / 138.9	0.494±0.063	6.55±0.02	12.46±1.46	420±49	442±56	1176±29 dDY	16.76±0.88 dDX	20.57±1.67 dDY
	3.2	1000 / 31.6	0.515±0.081	6.58±0.02	16.77±3.18	569±107	392±62	909±37 aDY	10.12±1.11 aEY	13.49±1.36 aEY
		2000 / 63.2	0.478±0.069	6.57±0.02	12.95±1.84	440±63	364±52	1086±16 bDY	12.30±1.14 bDY	15.84±1.79 bDY
		3000 / 94.7	0.526±0.064	6.57±0.01	13.61±1.61	462±55	401±49	1140±19 cDY	15.28±1.22 cDY	19.24±1.87 cDY
		4400 / 138.9	0.492±0.081	6.57±0.02	12.28±1.81	416±63	375±62	1180±23 dDY	17.21±1.14 dDY	21.09±1.79 dDY
	1.6	1000 / 31.6	0.485±0.047	6.57±0.01	15.49±1.76	525±61	351±34	926±47 aDY	9.77±0.61 aDEY	14.05±0.82 aEY
		2000 / 63.2	0.537±0.063	6.57±0.02	14.96±1.62	508±55	389±46	1057±32 bEY	13.18±0.84 bEY	18.04±1.34 bEY
		3000 / 94.7	0.469±0.042	6.56±0.01	10.44±1.71	416±40	340±31	1128±24 cDY	14.68±0.66 cDY	19.38±1.24 bDY
		4400 / 138.9	0.494±0.049	6.56±0.02	12.48±1.28	423±44	358±35	1171±27 dDY	18.31±1.30 dEY	23.91±2.49 cEY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); V - Compact volume; Vs – Void free compact volume; ¥ Total Specific Energy = Specific Energy for Compression + Specific Energy for Extrusion.

5.5.4 Specific Energy

Table 5.3-5.6 shows the total specific energy (MJ/t) required to form compacts from non-treated and steam exploded barley, canola, oat and wheat straw, which is obtained from the summation of specific energy required for compression and extrusion of a compacts. It is important to note that the specific energy values reported in this section are used to compare the densification variables. However, these values may not have practical application since the energy consumed by commercial densification machines may be higher than the values in this study.

In general, the total and compression specific energy for compaction of non-treated and steam exploded barley, canola, oat and wheat straw at any particular hammer mill screen size significantly increased with an increase in applied pressure and significantly decreased with a decrease in hammer mill screen size, with a few exceptions (Table 5.3-5.6).

The total and compression specific energy required for compacting steam exploded barley straw was significantly lower than non-treated straw at all screen sizes and pressures, except for steam exploded straw at 1.6 mm screen size for pressures of 31.6, 94.7 and 138.9 MPa, which were statistically similar (Table 5.3). Therefore, based on density and total specific energy data, it could be concluded that steam exploded barley straw for 3.2 mm screen size at a pressure of 138.9 MPa produced compacts having 13% higher density and consumed 19% lower total specific energy compared to non-treated straw. At this condition, the average extrusion energy is 0.01% of the total specific energy.

The total and compression specific energy required for compacting steam exploded canola straw was significantly higher than non-treated straw at all screen sizes and pressures, with a few exceptions (Table 5.4). Therefore, based on density and total specific energy data, it could be concluded that steam exploded canola straw for 1.6 mm screen size at a pressure of 138.9 MPa produced compacts having 13% higher density and consumed 22% higher total specific energy compared to non-treated straw. At this condition, the average extrusion energy is 16% of the total specific energy.

The total and compression specific energy required for compacting steam exploded oat straw was significantly higher than non-treated straw at all screen sizes and pressures, except for total specific energy for 6.4 mm screen size at 138.9 MPa and compression specific energy for 6.4

mm screen size at 63.2 MPa (Table 5.5). Therefore, based on density and total specific energy data, it could be concluded that steam exploded oat for 3.2 mm screen size at a pressure of 94.7 MPa produced compacts having 19% higher density and consumed 13% higher total specific energy compared to non-treated straw. At this condition, the average extrusion energy is 16% of the total specific energy.

The total and compression specific energy required for compacting steam exploded wheat straw was significantly higher than non-treated straw at all screen sizes and pressures, except for total specific energy for 6.4 mm screen size at 31.6 MPa and compression specific energy for 6.4 mm screen size at 94.7 and 138.9 MPa (Table 5.6). Therefore, based on density and total specific energy data, it could be concluded that steam exploded wheat straw for 6.4 mm screen size at a pressure of 138.9 MPa produced compacts having 17% higher density and consumed 17% higher total specific energy compared to non-treated straw. At this condition, the average extrusion energy is 19% of the total specific energy.

5.5.5 Fitting Compression Models to Pressure, Density and Volume Data

Three compression models were fitted to the pressure-volume and pressure-density data to analyze the compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw. Tables 5.7, 5.8 and 5.9 present the parameters obtained after curve fitting Jones (1960), Cooper-Eaton (1962) and Kawakita-Ludde (1971) models, respectively.

Jones (1960) derived a linear equation, which expressed the logarithmic value of density as a function of the logarithmic pressure. Low R^2 values were obtained when the Jones model was fitted to the pressure-density data (Table 5.7). However, the value of constant *m* provided valuable information about the onset of plastic deformation of the ground straw at relatively low pressure, thus, indicating that the material is more compressible. Higher *m* values of 0.178 (3.2 mm), 0.195 (3.2 mm), 0.176 (1.6 mm), 0.175 (3.2 mm) for non-treated barley, canola, oat and wheat straw, respectively were observed indicating they are more compressible at the specified screen size. Similarly, higher *m* values of 0.189 (3.2 mm), 0.219 (3.2 mm), 0.182 (6.4 mm), 0.186 (6.4 mm) for steam exploded barley, canola, oat and wheat straw, respectively. In general, based on the *m* values, it was concluded that steam exploded straw is more compressible than non-treated straw. The steam exploded canola straw at 3.2 mm hammer mill screen size has

observed to be more compressible than any other straw samples. The highest R^2 values of 0.92 (3.2 mm), 0.94 (1.6 mm), 0.92 (1.6 mm) and 0.91 (3.2 mm) were obtained for non-treated barley, canola, oat and wheat straw, respectively. Similarly, the highest R^2 values of 0.95 (1.6 mm), 0.91 (1.6 mm), 0.90 (1.6 mm) and 0.90 (6.4 mm) were obtained for steam exploded barley, canola, oat and wheat straw, respectively.

Table 5.8 gives the parameters obtained when the Cooper-Eaton model (1962) was fitted to the experimental data. The dimensionless coefficients, a_1 and a_2 represent the densification of powdered material by particle rearrangement and deformation, respectively. If the sum of coefficients ($a_1 + a_2$) is less than unity, it is an indication that other process must become operative before complete compaction is achieved. The a_1 values for non-treated and steam exploded barley, canola, oat and wheat straw were higher than a_2 values (except for steam exploded barley at 1.6 mm screen size), which indicates that material densified easily by particle rearrangement. The sum of coefficients ($a_1 + a_2$) for all non-treated and steam exploded straw at 6.4 mm screen size, non-treated barley straw at 3.2 mm, steam exploded canola straw at 3.2 mm and steam exploded wheat straw at 1.6 mm screen sizes were observed to be above unity. The phenomenon of having sum of coefficient more than unity was also observed by Adapa et al. (2002 and 2009), and Shivanand and Sprockel (1992), which implies that the densification could not be fully attributed to the two mechanisms of compression assumed by Cooper-Eaton (1962). The highest R^2 values of 0.93 (3.2 mm), 0.94 (1.6 mm), 0.94 (1.6 mm) and 0.95 (3.2 mm) were obtained for non-treated barley, canola, oat and wheat straw, respectively. Similarly, highest R^2 values of 0.96 (1.6 mm), 0.94 (1.6 mm), 0.95 (1.6 mm) and 0.94 (3.2 mm) were obtained for steam exploded barley, canola, oat and wheat straw, respectively.

In Table 5.8, the values of k_1 and k_2 represents the pressure required to induce particle rearrangement and deformation, respectively. However, negative values are contrary to application of compressive pressures. Similar observations were made by Tabil and Sokhansanj (1996) for compressing alfalfa grinds and by Shaw (2008) while compressing non-treated and steam exploded poplar and wheat straw grinds. Therefore, the validity of the model constants for these biomass feedstocks to represent their physical definition must be called into question.

It was observed that the Kawakita-Ludde model (Table 5.9) provided the best fit scenario having R^2 values of 0.99 for non-treated straw and 1.00 for steam exploded biomass samples. In

Kawakita-Ludde model, the constant *a* represents the initial porosity of the sample. Highest *a* values of 0.912, 0.866, 0.894, and 0.903 were obtained for non-treated barley, canola, oat and wheat straw at 6.4 mm screen size, respectively. Similarly, highest *a* values of 0.969, 0.976, 0.966 and 0.969 were obtained for steam exploded barley, canola, oat and wheat straw at 6.4 mm screen size, respectively (Table 5.9). Based on the above data, it can be deduced that the steam exploded straw have higher porosity than non-treated straw. The steam exploded canola straw at 6.4 mm hammer mill screen size was observed to have more porosity than any other straw samples, which corresponds to the highest geometric mean diameter (0.698±0.127 mm) among steam exploded samples (Table 5.1).

The parameter *1/b* in the Kawakita-Ludde model indicates the yield strength or failure stress of the compact (MPa) (Table 5.9). The highest *1/b* values of 2.295 (3.2 mm), 3.486 (1.6 mm), 3.174 (1.6 mm), and 2.040 (3.2 mm) were obtained for non-treated barley, canola, oat and wheat straw, respectively. Similarly, the highest *1/b* values of 0.997, 0.650, 0.742, and 1.091 were obtained for steam exploded barley, canola, oat and wheat straw at 1.6 mm screen size, respectively (Table 5.9). The steam exploded straw is easier to compress since it has lower yield strength or failure stress values compared to non-treated straw. The steam exploded canola straw at 1.6 mm hammer mill screen size was observed to have lower yield strength or failure stress than any other straw samples.

Table 5.7: Compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw using Jones Model $\ln \rho = \boldsymbol{m} \ln \boldsymbol{P} + \boldsymbol{b}$

Agricultural Biomass	Hammer Mill Screen Size (mm)	Constants		R^2 Values	SSE
		m (kg/N-m)	b (kg/m^3)		
Non-Treated					
Barley Straw	6.4	0.160	6.149	0.839	0.059
	3.2	0.178	6.062	0.920	0.034
	1.6	0.168	6.096	0.865	0.053
Canola Straw	6.4	0.155	6.178	0.685	0.134
	3.2	0.195	6.001	0.904	0.049
	1.6	0.178	6.064	0.935	0.027
Oat Straw	6.4	0.130	6.276	0.753	0.068
	3.2	0.133	6.243	0.857	0.036
	1.6	0.176	6.077	0.923	0.031
Wheat Straw	6.4	0.167	6.104	0.833	0.067
	3.2	0.175	6.067	0.908	0.037
	1.6	0.145	6.223	0.868	0.039
Steam Exploded					
Barley Straw	6.4	0.150	6.317	0.707	0.113
	3.2	0.189	6.140	0.916	0.040
	1.6	0.154	6.310	0.953	0.014
Canola Straw	6.4	0.212	6.025	0.897	0.062
	3.2	0.219	6.008	0.879	0.081
	1.6	0.158	6.295	0.907	0.031
Oat Straw	6.4	0.182	6.171	0.866	0.063
	3.2	0.150	6.325	0.859	0.045
	1.6	0.138	6.399	0.900	0.026
Wheat Straw	6.4	0.186	6.168	0.897	0.048
	3.2	0.178	6.217	0.894	0.045
	1.6	0.161	6.280	0.874	0.046

Table 5.8: Compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw using Cooper – Eaton Model $\frac{V_0 - V}{V_0 - Vs} = a_1 e^{-\frac{k_1}{P}} + a_2 e^{-\frac{k_2}{P}}$

Agricultural Biomass	Hammer Mill Screen Size (mm)	Constants				R^2 Values	SSE
		a_1	a_2	k_1 (MPa)	k_2 (MPa)		
Non-Treated							
Barley Straw	6.4	0.809	0.199	1.170	1.170	0.902	0.001
	3.2	0.912	0.097	0.701	22.519	0.932	0.001
	1.6	0.893	0.100	2.180	2.180	0.901	0.002
Canola Straw	6.4	0.816	0.200	1.900	1.900	0.801	0.003
	3.2	0.744	0.250	3.166	3.166	0.939	0.002
	1.6	0.806	0.173	7.680	-11.423	0.941	0.002
Oat Straw	6.4	0.827	0.200	1.139	1.139	0.839	0.001
	3.2	0.767	0.231	5.223	-7.446	0.871	0.001
	1.6	0.983	0.005	4.081	-58.910	0.939	0.002
Wheat Straw	6.4	0.802	0.200	1.384	1.384	0.880	0.001
	3.2	0.586	0.400	2.012	2.011	0.944	0.001
	1.6	0.820	0.159	1.804	1.804	0.930	0.001
Steam Exploded							
Barley Straw	6.4	0.706	0.300	0.370	0.370	0.812	0.000
	3.2	0.899	0.101	2.563	-10.492	0.928	0.000
	1.6	0.235	0.759	11.050	-1.553	0.960	0.000
Canola Straw	6.4	0.700	0.309	-0.640	3.056	0.909	0.000
	3.2	0.506	0.500	0.625	0.625	0.930	0.000
	1.6	0.600	0.399	0.656	0.656	0.940	0.000
Oat Straw	6.4	0.927	0.078	1.168	-6.457	0.892	0.000
	3.2	0.600	0.399	0.738	0.738	0.908	0.000
	1.6	0.593	0.400	0.785	0.785	0.951	0.000
Wheat Straw	6.4	0.700	0.305	0.465	0.465	0.923	0.000
	3.2	0.700	0.300	0.820	0.820	0.937	0.000
	1.6	0.867	0.128	2.898	-8.942	0.879	0.000

Note: The volume of compact at zero pressure (V_0) was calculated using the mass of pellet (Table 5.3-5.6) and bulk density of ground samples (Table 5.1)

Table 5.9: Compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw using Kawakita – Ludde Model $\frac{P}{C} = \frac{1}{ab} + \frac{P}{a}$

Agricultural Biomass	Hammer Mill Screen Size (mm)	Constants		R^2 Values	SSE
		a	1/b (1/MPa)		
Non-Treated					
Barley Straw	6.4	0.912	1.072	0.999	5.005
	3.2	0.869	2.295	0.999	8.282
	1.6	0.858	2.116	0.999	11.309
Canola Straw	6.4	0.866	1.337	0.999	26.573
	3.2	0.836	3.257	0.999	15.911
	1.6	0.822	3.486	0.999	15.127
Oat Straw	6.4	0.894	0.945	0.999	10.306
	3.2	0.853	1.847	0.999	17.181
	1.6	0.827	3.174	0.999	20.554
Wheat Straw	6.4	0.903	1.358	0.999	8.093
	3.2	0.873	2.040	0.999	7.915
	1.6	0.859	1.652	0.999	7.422
Steam Exploded					
Barley Straw	6.4	0.969	0.270	1.000	1.294
	3.2	0.944	0.923	1.000	1.737
	1.6	0.927	0.997	1.000	0.910
Canola Straw	6.4	0.976	0.442	1.000	0.481
	3.2	0.967	0.572	1.000	0.652
	1.6	0.948	0.650	1.000	0.787
Oat Straw	6.4	0.966	0.486	1.000	0.570
	3.2	0.938	0.678	1.000	0.826
	1.6	0.928	0.742	1.000	1.145
Wheat Straw	6.4	0.969	0.465	1.000	0.362
	3.2	0.944	0.777	1.000	0.773
	1.6	0.922	1.091	1.000	2.356

Note: The volume of compact at zero pressure (V_0) was calculated using the mass of pellet (Table 5.3-5.6) and bulk density of ground samples (Table 5.1)

5.6 Conclusions

The following conclusions could be drawn from this study:

1. For non-treated and steam exploded barley, canola, oat and wheat straw grinds, the pressure and pre-treatment were significant factors which affected the compact density.

2. Ground steam exploded barley straw at screen sizes of either 3.2 or 1.6 mm produced high density compacts, while ground steam exploded canola, oat and wheat straw at screen sizes of 6.4, 3.2 or 1.6 mm produced high density compacts.

3. In general, the steam exploded straw produced compacts having significantly higher density compared to non-treated straw. However, the steam exploded barley straw consumed significantly lower total specific energy; while steam exploded canola, oat and wheat straw consumed significantly higher total specific energy compared to non-treated straw, primarily due to higher extrusion specific energy.

4. Steam exploded straw was more compressible than non-treated straw. The steam exploded straw was easier to compress since it had lower yield strength or failure stress values compared to non-treated straw.

5. Kawakita-Ludde model provided the best fit to the experimental data having R^2 values of 0.99 for non-treated straw and 1.00 for steam exploded biomass samples. The steam exploded straw had higher porosity than non-treated straw.

Chapter 6

6. Pelleting Characteristics of Selected Biomass with and without Steam Explosion Pretreatment

A similar version of this chapter has been published in the International Journal of Agricultural and Biological Engineering:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2010. Pelleting characteristics of selected biomass with and without steam explosion pretreatment. *International Journal of Agricultural and Biological Engineering*, 3(3): 62-79.

During the course of Ph.D. research, the outcomes of pilot-scale pelleting experiments for non-treated and steam exploded agricultural straw were in-part also presented and published in two national and international conferences:

- Adapa, P.K., L.G. Tabil, G.J. Schoenau and A. Opoku. 2010. Pelleting of agricultural biomass with and without pre-treatment. 2nd Annual General Meeting, Cellulosic Biofuel Network Meeting, Agricultural and Bioproducts Innovation Program, Ottawa, ON, Poster No. 19, March 11-12, and Agricultural Biorefinery Innovation Network, Agricultural and Bioproducts Innovation Program, London, ON, March 15-16.
- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2010. Feasibility study on the pelletization of barley, canola, oat and wheat straw grinds. ASABE Annual International Meeting, Pittsburgh, Pennsylvania, USA, Paper No. 1009141, June 20-23. St. Joseph, MI: ASABE.

Contribution of Ph.D. Candidate

Baseline data for change in density and durability were developed that can be used by manufacturer of pellets to perform relative comparison of quality of pellets manufactured from non-treated and steam exploded agricultural straw at various hammer mill screen sizes. In addition, a procedure for pilot-scale pelleting of non-treated and steam exploded straw was successfully developed and practical problems related to flowability of grinds through pellet mill and production of high quality pellets were identified. Customization of straw was explored to enhance the natural binding capability of steam exploded straw mixed at different proportions with non-treated straw resulting in high density and durability pellets. Pilot-scale energy requirement was established, which is more practical for energy calculations and design of large-scale biofuel pelleting operations. Experimental design, data analysis, and writing of journal articles were performed by Phani Adapa, while Dr. Lope Tabil and Dr. Greg Schoenau reviewed the experimental plan, suggested strategies for pelleting of biomass in the pilot-scale pellet mill and provided editorial input. Mr. Anthony Opoku provided technical assistance during pilot-scale pelleting process.

Contribution of these Papers to Overall Study

Knowledge Gap: After a thorough literature review, it was determined that there is a dearth of knowledge related to quality factors (density and durability) associated with densification of non-treated and steam exploded agricultural biomass and their relative comparison. In addition, literature on pilot scale pelleting of agricultural straw is scarce. Therefore, the objectives were: a) to determine the effect of pressure and biomass grind size on the density and durability of pellets and also the change in pellet density during storage from non-treated and steam exploded barley, canola, oat and wheat straw grinds; and b) to produce high density and high durability pellets from ground non-treated and steam exploded barley, canola, oat and wheat straw using a pilot-scale pellet mill.

Justification: The quality of fuel pellet is usually assessed based on its density and durability. High bulk density increases storage and transport capacity of pellets. Since feeding of boilers

and gasifiers generally is volume-dependent, variations in bulk density should be avoided (Larsson et al., 2008). A bulk density of 650 kg/m^3 is stated as design value for wood pellet producers (Obernberger and Thek, 2004). Low durability of pellets results in problems like disturbance within pellet feeding systems, dust emissions, and an increased risk of fire and explosions during pellet handling and storage (Temmerman et al., 2006).

Raw materials causing uneven pellet production have low bulk density compared to other milled biofuel pellet raw materials. Low raw material bulk density will put higher demands on the die feeding system of the pelletizer with greater volume throughput for maintained production level.

It has been successfully demonstrated that pre-treated agricultural biomass at lab-scale significantly improves pellet quality (density and durability) (Chapter 5); however, these results do not translate directly to pilot-scale pelleting while posing practical manufacturing constraints. Non-treated agricultural biomass was successfully pelletized with some modifications to the process parameters. Steam exploded biomass can be used as a natural binder for non-treated biomass to form pellets with high durability values. There is a need to design new pilot-scale pelleting technology and development of new procedure since existing technology seems to over-work on the low bulk density straw and results in clogging of pellet mill. Alternatively, pre-compression of straw grinds needs to be investigated as an alternative to increase their bulk density and flowability through the pellet mill. In addition, steam conditioning of higher grind sizes should be explored that could result in production of pellets. However, an overall energy balance study is required to determine a trade-off between using steam conditioning or pre-compression vs. energy saved during hammer mill grinding of straw to large grind sizes.

6.1 Abstract

Biomass pelleting experiments were designed to conduct single-pelleting of non-treated and steam exploded barley, canola, oat and wheat straw grinds obtained from 6.4, 3.2, and 1.6 mm hammer mill screen sizes by applying pressures of 31.6, 63.2, 94.7, and 138.9 MPa using a close-fit plunger die assembly (die length 135.3 mm and diameter of 6.30±0.5 mm). Subsequently, pilot scale pelleting of non-treated and steam exploded straw was performed based

on the conclusions derived from single-pelleting experiments. The quality of pellets from close-fit plunger die assembly was ascertained by measuring their respective density and durability. In addition, change in pellet density was measured after a storage period of one month to ascertain its dimensional stability. The density of pellets from non-treated and steam exploded agricultural straw significantly increased with an increase in applied pressure at any specific hammer mill screen size. The pellet density of steam exploded straw grinds at any specific hammer mill screen size and pressure was significantly higher than non-treated straw grinds. At any specific hammer mill screen size, the durability of pellets from non-treated straw grinds did not show any significant change with an increase in applied pressures. However, durability of pellets from non-treated straw grinds significantly decreased with a decrease in hammer mill screen size from 6.4 to 1.6 mm at any specific applied pressure. High durability values (>80%) were observed for pellets of non-treated straw grinds at 6.4 mm hammer mill screen size and for pellets from steam exploded straw grinds at all hammer mill screen sizes and applied pressure levels.

During pilot scale pelleting, customization of grounds straw material was also performed by adding steam exploded biomass in increments of 25% to non-treated ground straw for respective biomass at specific grind size. In addition, the straw samples were ground using 0.8 mm hammer mill screen size to improve their flowability through the pellet mill. Subsequently, the straw samples were conditioned to 17.5% moisture content and 10% flaxseed oil content to increase the bulk density and flowability of grinds, which resulted in the production of pellets. The steam conditioning of straw grinds during pelleting was not performed in order to minimize energy input. The pellet mill produced pellets from ground non-treated straw at hammer mill screen sizes of 0.8 and 1.6 mm and customized samples having 25% steam exploded straw at 0.8 mm. However, the steam exploded ground straw did not produce pellets. In general, density of pellets increased with a decrease in screen size from 1.6 to 0.8 mm. However, no significant differences in density values were observed for non-treated samples at 0.8 mm and customized samples. Bulk density of straw pellets significantly varied with grind size and customization, and was found highest for customized straw. The durability of pellets significantly increased with a decrease in grind size for non-treated samples from 1.6 to 0.8 mm. However, the addition of steam exploded straw to non-treated straw at 0.8 mm screen size significantly decreased the durability. The durability of pellets was negatively correlated to pellet mill throughput and was positively correlated to specific energy consumption.

6.2 Introduction

The two main sources of biomass for energy generation are purpose-grown energy crops and waste materials (Larkin et al., 2004). Energy crops, such as Miscanthus and short rotation woody crops (coppice), are cultivated mainly for energy purposes and are associated with the food vs. fuels debate, which is concerned with whether land should be used for fuel rather than food production. The use of residues from agriculture, such as barley, canola, oat and wheat straw, for energy generation circumvents the food vs. fuel dilemma and adds value to existing crops (Chico-Santamarta et al., 2009; The German Solar Energy Society, 2005).

The main problem with straw is its relatively low density in its original or baled forms. The bulk density of loose and standard baled straw is approximately 40 kg/m^3 and 100 kg/m^3, respectively, compared with the bulk density of unprocessed wood residue, which is approximately 250 kg/m^3 (Demirbas, 2001; Tripathi et al., 1998). The relative low density of straw makes it more expensive to transport compared to wood and coal because a lower mass of straw can be transported per unit volume. Additionally, a larger storage area/volume is required for baled straw compared to wood chip. Densification into pellets increases the bulk density of biomass (McMullen et al., 2005; Obernberger and Thek, 2004) and as a result, the net calorific content per unit volume is increased (Bhattacharya et al., 1989) and the storage, transport and handling of the material is easier and cheaper (Bhattacharya et al., 1989; Balatinecz, 1983; Kaliyan and Morey, 2006a).

The quality of fuel pellet is usually assessed based on its density and durability. High bulk density increases storage and transport capacity of pellets. Since feeding of boilers and gasifiers generally is volume-dependent, variations in bulk density should be avoided (Larsson et al., 2008). A bulk density of 650 kg/m^3 is stated as design value for wood pellet producers [7]. Low durability of pellets results in problems like disturbance within pellet feeding systems, dust emissions, and an increased risk of fire and explosions during pellet handling and storage (Temmerman et al., 2006).

Raw materials causing uneven pellet production have low bulk density compared to other milled biofuel pellet raw materials. Low raw material bulk density will put higher demands on the die feeding system of the pelletizer with greater volume throughput for maintained production level. Temmerman et al. (2006) investigated the pre-compaction of straw as an alternative to avoid low and intermittent production of pellets. Pressurized steam conditioners are used in the feed pellet industry to decrease raw material porosity and to improve pellet hardness/ durability (Thomas et al., 1997).

The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). It is postulated that by disrupting the lignocellulosic biomass materials via steam explosion pretreatment, the compression and compaction characteristics can be improved (Shaw, 2008). Zandersons et al. (2004) stated that activation of lignin and changes in the cellulosic structure during the steam explosion process facilitate the formation of new chemical bonds. Lam et al. (2008) reported that the quality (durability) of pellets produced from steam exploded sawdust was 20% higher than non-treated sawdust.

In addition, the application of pretreatment operations such as size reduction/ grinding is a critical in order to increase the surface area of the material prior to densification (Mani et al., 2004). Particle size reduction increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process (Drzymala, 1993).

Traditionally, steam conditioning of biomass has been performed to increase flowability of grinds through pellet mill and enhance its natural binding capability (Tabil and Sokhansanj, 1996). The steam conditioning of straw grinds during pilot scale pelleting was not considered as an option in order to minimize energy input (Shaw et al., 2007). Previously, some work had been reported by Mani et al. (2006 a and b) on mechanical properties of ground barley and wheat straw and by Shaw (2008) on ground non-treated and steam exploded wheat straw as a feedstock for biofuel industry. However, there is a dearth of knowledge related to quality factors (density and durability) associated with densification of non-treated and steam exploded agricultural biomass and their relative comparison. In addition, literature on pilot scale pelleting of agricultural straw is scarce. Therefore, the objectives of this study are:

1) To determine the effect of pressure and biomass grind size on the density and durability of pellets from non-treated and steam exploded barley, canola, oat and wheat straw grinds using a single-pelleting apparatus having a close-fit plunger die assembly. In addition, change in pellet density during storage was studied; and

2) The conclusions obtained from objective one are used as a guide to produce high density and high durability pellets from ground non-treated and steam exploded barley, canola, oat and wheat straw using a pilot scale pellet mill.

6.3 Materials and Methods

6.3.1 Agricultural Biomass

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used in the experiments. The straw samples were acquired in small square bale form (typically having dimensions of 0.45 x 0.35 x 1.00 m) during the summer of 2008 from a farmer in the Central Butte area of Saskatchewan, Canada.

The initial moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3, and 4.0% (wb), respectively. The agricultural biomass was stored under a tarpaulin cover during the winter of 2008 (approximately for 7 months). During this period, the moisture content of barley, canola, oat and wheat straw was increased to 13.5, 15.1, 13.1, and 15.6% (wb), respectively.

All of the baled straw samples were chopped using a chopper, which was fabricated in the Bioprocessing Lab, Department of Agricultural and Bioresource Engineering, University of Saskatchewan, Canada. The biomass chopper has six blades; each fixed at a shearing angle of 14^{o} and rotated at 460 rpm. The chopped biomass was subsequently ground using a hammer mill (Serial no. 6M13688; 230 Brookdale, St. Maywood, NJ) having 22 swinging hammers, attached to a shaft powered by a 1.5 kW electric motor. The shaft was allowed to rotate at 3800 rpm. Five screen sizes of 30, 6.4, 3.2, 1.6, and 0.8 mm were used to grind the non-treated biomass. A dust collector (House of Tools, Model no. DC-202B, Saskatoon, SK) having a 9 A suction fan

rotating at 3500 rpm was connected to the outlet of the hammer mill to control dust during operation, provide flowability of chopped biomass through the hammer mill, and collect the ground biomass. A portion (25 kg) of each of the biomass ground in the hammer mill using 30 mm screen was sent to FPInnovations in Quebec City, Quebec for steam explosion pretreatment.

6.3.2 Steam Explosion of Agricultural Biomass

The steam explosion of ground straw obtained using 30 mm hammer mill screen size was performed at the pilot-scale continuous steam explosion plant of FPInnovations, Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized refiner having a plate gap of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive was set to operate at 2000 rpm. The throughput of the equipment can vary between 50 and 200 kg of dried material per hour, depending on the bulk density of the raw material and the desired final particle size of the steam exploded material. The feed rate of agricultural straw into the digester was controlled using a plug screw feeder. The digester was operated at 180^{o}C (steam pressure of 900 kPa) for 4 min to perform steam explosion pretreatment of the agricultural biomass. A flash tube convective dryer having a 90 m long tube was used to dry the steam exploded barley, canola, oat and wheat straw having an average moisture content of 70.1, 80.7, 76.7, and 81.0% (wb) to approximately an average moisture content of 12.2, 13.6, 12.0, and 12.0% (wb), respectively. The direct heating of air was performed using 1172 kW (4 million BTU/h) natural gas burner, which has variable control to operate at different temperatures.

During the transportation of steam exploded material from Quebec City, Quebec to Saskatoon, Saskatchewan, the average moisture content of steam exploded barley, canola, oat and wheat straw further decreased to 7.8, 6.2, 6.8, and 7.0 % (wb), respectively. The steam exploded material was further ground in a hammer mill using four screen sizes of 6.4, 3.2, 1.6, and 0.8 mm following the procedure described in the previous section.

In addition, prior to pilot scale pelleting, customization of grounds straw material was performed by adding steam exploded biomass (e.g. barley 0.8 mm grind size) in increments of 25% (up to a maximum of 50%) to non-treated ground straw (e.g. barley 0.8 mm grind size) for respective biomass at specific grind size.

6.3.3 Moisture Content

The moisture content of baled straw and steam exploded biomass was determined using ASABE S358 (ASABE, 2006a), where 25 g of material was oven-dried at 103^{o}C for 24 h. The moisture content of ground straw at hammer mill screen sizes of 6.4, 3.2, 1.6 and 0.8 mm was determined using AACC Standard 44-15A (AACC, 2005), where 2-3 g of material was oven-dried at 130^{o}C for 90 min. All of the moisture content tests were performed in replicates of three.

6.3.4 Particle Size Analysis

The geometric mean particle diameter of ground non-treated and steam exploded agricultural straw samples was determined using ASABE Standard S319 (ASABE, 2006b). Due to the low bulk density of steam exploded straw, only 50 g of ground sample (instead of 100 g) was placed on a stack of sieves arranged from the largest to the smallest opening. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used for particle size analysis. The sieve series selected were based on the range of particles in the samples. For grinds from 6.4 mm hammer mill screen opening, U.S. sieve numbers 10, 16, 20, 30, 50, and 70 (sieve opening sizes: 2.000, 1.190, 0.841, 0.595, 0.297, and 0.210 mm, respectively) were used. For grinds from 3.2, 1.6, and 0.8 mm hammer mill screen openings, U.S. sieve numbers 16, 20, 30, 50, 70, and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210, and 0.149 mm, respectively) were used. A 10 min sieve shaking time was used as suggested in the ASABE Standard S319. The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated in replicates of three for each straw samples.

6.3.5 Bulk and Particle Density of Biomass

Bulk density of hammer mill ground non-treated and steam exploded agricultural straw at four screen sizes of 6.4, 3.2, 1.6, and 0.8 mm was determined by carefully filling a standard 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB) with sample. After filling every third portion of the container with ground straw sample, it was tapped on a wooden table for approximately 10 times to allow the material to settle down. After completely filling the container, excess material at the top was removed by moving a steel roller in a zig-zag pattern. The mass per unit volume gave the bulk density of the biomass in kg/m^3. A gas multi-

pycnometer (QuantaChrome, Boynton Beach, FL) was used to determine the particle density of the hammer mill ground straw by calculating the displaced volume of nitrogen gas by a known mass of material, following the method reported by Adapa et al. (2005). Three replicates for each sample were performed for both bulk and particle density measurements.

6.3.6 Chemical Composition and Higher Heating Values

The chemical composition analysis of non-treated and steam exploded barley, canola, oat and wheat straw was performed in duplicates by the SunWest Food Laboratory Ltd., Saskatoon, SK, Canada, and the Feed Innovation Centre, University of Saskatchewan. Crude protein, crude fat, starch, lignin, acid detergent fibre (ADF), neutral detergent fibre (NDF) and total ash contents were determined using standard methods. The crude protein content of the biomass was determined using the AOAC standard method 2001.11 (AOAC, 2001), where the nitrogen content was multiplied by a factor of 6.25. The crude fat was determined using AOCS standard method Am2-93 (AOAC, 1999). Total starch content was measured using AOAC standard method 996.11 (AOAC, 1998). The lignin and ADF were determined using AOAC standard method 973.18 (AOAC, 1990a), whereas NDF was determined using AOAC standard method 992.16 (AOAC, 1990b). The total ash content was determined using AOAC standard method 942.05 (AOAC, 1990c). The cellulose percentage was calculated indirectly from percentage acid detergent fibre (ADF) and lignin (%ADF minus %lignin) (Mani et al., 2006a). Hemicellulose percentage was calculated indirectly from the percentages of neutral detergent fibre (NDF) and ADF (%NDF minus %ADF) (Mani et al., 2006a).

The calorific (heating) value of biomass feedstocks are indicative of the energy they possess as potential fuels. The gross calorific value (higher heating value, HHV) and the net calorific value (lower heating value, LHV) at constant pressure measures the enthalpy change of combustion with and without water condensed, respectively [34]. A Parr 1281 automatic isoperibol oxygen bomb calorimeter (Parr Instrument Company, Moline, IL) was used to determine the HHV of the non-treated and steam exploded straw in MJ/kg at the Feed Innovation Centre, University of Saskatchewan. ASTM Standard D5865-03 (ASTM, 2003) test method for gross calorific value of coal and coke, was used as a guideline for heating value testing.

6.3.7 Single-Pelleting Apparatus

A single-pelleting apparatus having a close fit plunger die assembly (Adapa et al., 2007) was used to study the compression characteristics of selected agricultural straw (Adapa et al., 2002). The cylindrical die was 135.3 mm long and 6.30±0.5 mm in diameter. A thermal compound (Wakefield Engineering Inc., Wakefield, MA) was coated on the outer surface of the die prior to wrapping the outer surface with copper shim stock. A dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, IL) was then wound evenly around the shim stock to provide the necessary heat. One type-T thermocouple, connected to the outer surface of the cylinder, was linked to a temperature controller to regulate the power input to the heater, thus allowing temperature control of the cylinder. Another type-T thermocouple was also connected to the outer cylinder wall, allowed verification of the cylinder temperature via a digital thermocouple reader (Shaw, 2008). The die was fitted on a stainless steel base having a hole matching its outer diameter. This gave stability and allowed the plunger to move straight down with no lateral movement. The plunger was attached to the upper moving crosshead of the Instron Model 1011 testing machine (Instron Corp., Canton, MA).

6.3.8 Single-Pelleting Test

Prior to the single-pelleting experiments, the biomass was re-moistened to 10% moisture content (wb) by adding/sprinkling a calculated amount of water to non-treated and steam exploded straw grinds at 6.4, 3.2, and 1.6 mm hammer mill screen sizes. The samples were subsequently stored in plastic bags and kept in a cold room at 4^{o}C for a minimum of 72 h. Only one moisture level of 10% (wb) was used based upon literature review to produce high density and durability pellets/briquettes from various straw and biomass (Kaliyan and Morey, 2006a and 2007; Mani et al., 2006a; Obernberger and Thek, 2004; Shaw and Tabil, 2007; Stevens, 1987).

The single-pelleting apparatus was used to make a single pellet in one stroke of the plunger from ground straw samples. In order to simulate frictional heating during commercial pelleting operation, the pelleting die was maintained at a temperature of 95±1^{o}C (Adapa et al., 2007; Mani et al., 2006b). The mass of samples used for making pellets varied between 0.5 and 0.7 g. Compressive force was applied using the Instron Model 1011 testing machine fitted with a 5000 N load cell and a 6.25 mm diameter plunger. Four preset loads of 1000, 2000, 3000 and 4400 N

corresponding to pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were used to compress samples in the die. The crosshead speed of the Instron testing machine was set at 50 mm/min. After compression, the plunger was retained in place for 30 s once the preset load was attained in order to avoid spring-back effect of biomass grinds (Adapa et al., 2007; Mani et al., 2006b). Later, the base plate was removed and the pellet was ejected out of the die by using the plunger.

6.3.9 Pilot Scale Pelleting

A laboratory scale CPM CL−5 pellet mill (California Pellet Mill Co., Crawfordsville, IN) was used for processing of non-treated and steam exploded agricultural straw grinds into pellets. The pellet mill consisted of a corrugated roller (diameter 85.0 mm) and ring die assembly. The ring die size (radius) and length (thickness) were 125.3 and 44.6 mm, respectively. The ring hole diameter and l/d ratio were 6.10 mm and 7.31, respectively. The rotational speed of the pellet mill was 250 rpm. All of the above specifications were adopted from previous studies performed by Tabil and Sokhansanj (1996), Adapa et al. (2004), and Hill and Pulkinen (1988) to produce high quality pellets from biomass.

At the onset of pelleting experiments, 2 kg each of ground non-treated barley, canola, oat and wheat straw grinds from 6.4, 3.2, and 1.6 mm hammer mill screen size were re-moistened to 10% moisture content (wb) by adding/ sprinkling a calculated amount of water and mixed a rotating concrete mixer. Only one moisture level of 10% (wb) was used based upon literature review to produce high density and quality pellets/briquettes from various straw and biomass (Kaliyan and Morey, 2006a and 2007; Mani et al., 2006a; Obernberger and Thek, 2004; Shaw and Tabil, 2007; Stevens, 1987). Due to low bulk density and poor flowability of ground straw, the pellet mill continuously clogged without producing any pellets. The non-treated and steam exploded straw was ground using 0.8 mm hammer mill screen size to improve the flowability of straw grinds. As pre-compaction (Larsson et al., 2008) and steam addition (Thomas et al., 1997) are energy intensive operations, it was decided to add both moisture and flax seed oil in incremental steps of 0.5% to further increase the bulk density and flowability of ground straw through pellet mill. Addition of moisture and oil to a level of 17.5% and 10%, respectively, resulted in production of pellets. Similar process was repeated for customized ground straw obtained from 6.4, 3.2, 1.6, and 0.8 mm hammer mill screen sizes.

The feed rate of material to the pellet mill was controlled using a vibratory feeder. Each successful pilot scale pelleting test was performed for an average period of 10 min. During this period, manufactured pellets were collected and weighed to determine the pellet mill throughput (kg/h). In addition, the pellet mill energy consumption (kWh) was recorded in real time using a data logger connected to a computer and was used to calculate the specific energy (MJ/t) required to manufacture pellets from respective agricultural biomass. The manufactured pellets were allowed to dry in ambient condition for 24 hr and subsequently stored in black plastic bags for at least 2 weeks prior to pellet density and durability tests.

6.3.10 Pellet Density, Bulk Density and Durability

Single-Pelleting Test: The mass, length and diameter of pellets were measured to determine the density in kg/m^3, following the extrusion of the pellets. Ten replicates (pellets) were made using each ground straw samples. Similar process was followed to determine the change in pellet density (% expansion) after a storage period of one month. The durability of pellets is usually measured following the ASABE Standard S269 (ASABE, 2007), which requires about 50-100 g of pellets/ compacts. However, due to limited number of pellets, it was not feasible to use this test. Instead, the durability of pellets was measured by following the drop test method (Al-Widyan and Al-Jalil, 2001; Khankari et al., 1989; Sah et al., 1980; Shrivastava et al., 1989), where a single pellet was dropped from a 1.85 m height on a metal plate. The larger intact portion of the mass retained is expressed as the percentage of the initial weight. Each drop test was replicated 10 times.

Pilot Scale Pelleting: The mass, length and diameter of individual pellets were measured to determine pellet density in kg/m^3. Ten pellets were selected from respective biomass samples. The bulk density of manufactured pellets was calculated by measuring the mass of pellets filled in a 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB). Three replicates of bulk density measurements were performed for each biomass sample.

The durability of pellets was measured following the ASABE Standard S269 (ASABE, 2007). A 100 g of pellet sample was weighed and placed in a dust-tight enclosure/ chamber, and tumbled for 10 min at 50 rpm. A 5.70 mm sieve was used to determine the fines produced by the pellets during the tumbling process. The mass of pellets left on the sieve, as percentage of the total mass

of pellet sample used during the test, was considered as the durability of the pellets. Three replicates of the durability test were performed for each sample.

6.3.11 Statistical Analysis

The experiments were set up as completely randomized experimental design with density and durability as the dependent variables, and straw type, pre-treatment, hammer mill screen size and pressure as the independent variables. Statistical analyses were conducted using SAS for Windows (version 8.2) (SAS, 1999). In order to further understand and explain the experimental variables and their interactions, the SAS general linear model (GLM) for completely randomized design (CRD) procedure was used and the Student-Neuman-Keuls test (SNK) was performed. SNK determines the difference between any two treatment means at 5% level of significance (SAS, 1999).

6.4 Results and Discussion

6.4.1 Geometric Mean Particle Size

Table 5.1 (Chapter 5) shows the mean geometric particle diameters for non-treated and steam exploded barley, canola, oat and wheat straw. The mean geometric particle diameter for any particular biomass decreased with a decrease in hammer mill screen size from 6.4 to 0.8 mm. The non-treated wheat straw at 6.4 mm and canola straw at 0.8 mm resulted in largest (0.997±0.038 mm) and smallest (0.340±0.003 mm) mean particle diameters, respectively, while for steam exploded straw, the largest and smallest geometric mean diameter of 0.698±0.127 mm and 0.296±0.013 mm were obtained for canola at 6.4 mm and barley at 0.8 mm hammer mill screen sizes, respectively.

The geometric mean particle diameter of steam exploded straw grinds at any specific hammer mill screen size was significantly smaller than non-treated straw grinds. This could be due to the fact that steam explosion pre-treatment disintegrated the lignocellulosic structure of the biomass leading to lower shear strength (easier to grind the straw).

6.4.2 Bulk Density

The bulk density values for barley, canola, oat and wheat straw grinds are given in Table 5.1. The bulk density of non-treated and steam exploded straw significantly increased with a decrease in hammer mill screen size from 6.4 to 0.8 mm. For non-treated straw, the highest bulk density of 247±05 kg/m^3 was obtained for canola straw grinds at 0.8 mm hammer mill screen size, while lowest bulk density of 96±02 kg/m^3 was obtained for barley straw grinds at 6.4 mm hammer mill screen size. For steam exploded straw, the highest and lowest bulk densities were obtained for wheat straw (138±03 kg/m^3) at 0.8 mm screen size and canola straw (33±02 kg/m^3) at 6.4 mm screen size, respectively.

The bulk density of non-treated barley, canola, oat and wheat straw at any specific hammer mill screen size was significantly higher than steam exploded straw (Table 5.1). This could again be attributed to the fact that steam explosion pre-treatment disintegrates the organized and compact lignocellulosic structure of biomass leading to lower bulk densities. This low bulk density of steam exploded straw grinds could be problematic in pelletizing the biomass as discussed later.

6.4.3 Particle Density

In general, the particle density of non-treated and steam exploded canola and oat straw significantly increased with a decrease in hammer mill screen size from 6.4 to 0.8 mm (Table 5.1). For non-treated straw, the highest particle density of 1370±07 kg/m^3 was obtained for wheat straw at 0.8 mm and lowest particle density of 873±18 kg/m^3 was obtained for oat straw at 6.4 mm screen size. For steam exploded straw, the highest and lowest particle densities were obtained for barley (1449±82 kg/m^3) straw at 0.8 mm and canola (968±38 kg/m^3) straw at 6.4 mm screen sizes, respectively. The grinds obtained from smaller screen size will have less pore volume than larger particles, resulting in higher particle densities (Mani et al., 2004).

The particle density of steam exploded barley, canola, oat and wheat straw at any specific hammer mill screen size was significantly higher than non-treated straw, except for barley straw at 6.4 mm screen size, canola and wheat straw at 6.4 and 0.8 mm. This could be due to application of steam explosion pretreatment, which disintegrated the long chain lignocellulosic

structure into short chains leading to lower geometric particle sizes and consequently resulting in higher particle densities (Mani et al., 2004).

6.4.4 Chemical Composition and Higher Heating Values (HHV)

Table 5.2 (Chapter 5) enumerates the average chemical composition of non-treated and steam exploded barley, canola, oat and wheat straw samples for tests performed in duplicates. The non-treated canola straw had the highest protein content (6.53%); barley straw had the highest level of fat (1.91%) and lignin (17.13%), while wheat straw showed the highest levels of starch (2.58%) and ash (2.36%) contents. The steam exploded canola straw had the highest protein content (2.21%), canola straw has the highest level of lignin content (12.04%), barley straw had the highest level of starch content (0.38%) and ash content (3.62%). Non-treated canola and wheat straw showed the highest level of cellulose (42.39%) and hemicelluloses content (23.68%), respectively, while steam exploded oat and barley straw showed highest level of cellulose (47.52%) and hemicelluloses (26.49%), respectively.

Traditionally, steam explosion is accepted as one of the most attractive and cost-effective methods for hardwoods and straws to enhance the cellulose susceptibility to enzymatic attack during fermentation process (Jin and Chen, 2006) by destruction of hemicelluloses and incomplete disruption of lignin–carbohydrate matrix. During the steam explosion process, pressurized steam disintegrates the lignocellulosic structure of the straw, and hydrolyses the lignin and hemicellulose content; a portion which is washed and drained with waste water. Therefore, the percentage of lignin and hemicellulose in dry steam exploded straw was lower than non-treated straw, thus increasing the relative percentage of cellulose content (Table 5.2).

Cellulose, hemicelluloses and lignin are major components of plant biomass. Therefore, a change in their composition could potentially lead to a change in the HHV of the biomass. The cellulose content of steam exploded barley, canola, oat and wheat straw was 37, 7, 26 and 36% higher than non-treated straw, respectively. The hemicelluloses content of steam exploded barley, canola and oat straw was 30, 6 and 9% higher; however wheat straw was 14% lower than non-treated straw, respectively. The lignin content of steam exploded barley, canola, oat and wheat straw was 50, 15, 25 and 14% lower than non-treated straw, respectively. These observations were contrary to Shaw (2008) where a decrease in cellulose and hemicelluloses

content and an increase in lignin content of steam exploded poplar wood and wheat straw were reported. This could be due to the fact that they have performed the steam explosion at 200-205^{o}C for 4-5.5 min as opposed to the present study in which steam explosion was performed at 180^{o}C for 4 min.

The net combined percentage change of cellulose, hemicelluloses and lignin in steam exploded barley, canola, oat and wheat straw is 17, -2, 10 and 8% higher than non-treated straw, respectively. As a result, the average HHV of steam exploded barley, canola, oat and wheat straw was 6, 10, 9, and 5% higher than non-treated straw, respectively (Table 5.2). An increase in HHV for steam exploded canola straw could be due to a 4% decrease in ash content. Similar observations of increased HHV with a decrease in ash content was reported by Shaw (2008) and Sheng and Azevedo (2005).

6.4.5 Single-Pellet Density

In general, the density of pellets (subsequent to single-pelleting experiments) from non-treated and steam exploded agricultural straw significantly increased with an increase in applied pressure at any specific hammer mill screen size (Tables 6.1, 6.2, 6.3 and 6.4). An increase in pressure results in plastic deformation of ground particles and consequently leads to pellets that have densities closer to their respective particle densities (Table 5.1). There was no significant difference in pellet density obtained from different hammer mill screen sizes for non-treated and steam exploded straw at higher pressures of 94.7 and 138.9 MPa. This could be due to the fact that the pellet density at 94.7 MPa approached near to their respective particle densities (Table 5.1) and any higher pressure (138.9 MPa) did not account for significant increase in pellet density (Tables 6.1, 6.2, 6.3 and 6.4). The pellet density of steam exploded straw at any specific hammer mill screen size and pressure was significantly higher than non-treated straw. This observation can be directly related to significantly lower geometric mean particle diameters and significantly higher particle densities of steam exploded grinds compared to non-treated grinds.

Tables 6.1, 6.2, 6.3 and 6.4 also give the densities of pellets measured after one month of storage period to ascertain its dimensional stability, and associated handling and storage costs. A reduction in pellet density is usually expected due to relaxation of grinds in the pellet after release of pressure. For both non-treated and steam exploded straw, it has been observed that the

relaxation was higher for larger hammer mill screen sizes and lower applied pressures, with a very few exceptions usually having higher standard deviations in the measured densities. In some cases the average reduction in density was negative giving the impression that the pellet density actually increased during storage period. However, these negative values are primarily due to higher standard deviations in pellet density measurements. Therefore, from a practical manufacturing point of view, these values should be considered as a zero percent change in pellet density.

Due to limited number of pellets, it was not feasible to measure the bulk density of pellets; therefore, this was not undertaken.

Table 6.1: Measured pellet density and durability data for non-treated and steam exploded barley straw at 10% moisture content (wb).

Barley Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Pellet Density (kg/m^3)		Durability (%)[§]
			After Pelleting	After One Month	
Non-Treated	6.4	1000 / 31.6	798±19 aDX[£]	791±38	93±03 aDX
		2000 / 63.2	934±40 bDX	933±48	98±03 bDX
		3000 / 94.7	991±24 cDX	999±58	97±02 bDX
		4400 / 138.9	1003±32 cDX	947±52	97±02 bDX
	3.2	1000 / 31.6	788±27 aDX	726±46	61±08 aEX
		2000 / 63.2	915±28 bDX	876±48	73±10 bEX
		3000 / 94.7	976±18 cDX	973±39	83±06 cEX
		4400 / 138.9	1024±25 dDX	1033±29	63±06 aEX
	1.6	1000 / 31.6	781±38 aDX	750±73	49±10 aFX
		2000 / 63.2	914±19 bDX	897±42	50±09 aFX
		3000 / 94.7	972±12 cDX	967±22	50±07 aFX
		4400 / 138.9	994±28 cDX	1001±31	51±04 aFX
Steam Exploded	6.4	1000 / 31.6	903±43 aDY	875±32	90±07 aDX
		2000 / 63.2	1081±24 bDY	1045±29	96±03 aDX
		3000 / 94.7	1131±25 cDY	1150±28	97±03 aDX
		4400 / 138.9	1116±62 bcDY	1017±132	98±02 bDX
	3.2	1000 / 31.6	882±32 aEY	875±49	81±13 aDY
		2000 / 63.2	1022±28 bEY	1031±43	89±05 abEY
		3000 / 94.7	1130±22 cDY	1150±17	93±03 bEY
		4400 / 138.9	1159±35 dEY	1172±29	89±06 abEY
	1.6	1000 / 31.6	931±21 aDEY	935±23	86±05 abDY
		2000 / 63.2	1053±18 bFY	1057±18	81±05 bcFY
		3000 / 94.7	1112±23 cDY	1139±28	79±06 cFY
		4400 / 138.9	1169±12 dEY	1194±24	89±06 aEY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); § drop test was used to determine single pellet durability.

Table 6.2: Measured pellet density and durability data for non-treated and steam exploded canola straw at 10% moisture content (wb).

Canola Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Pellet Density (kg/m^3)		Durability (%)[§]
			After Pelleting	After One Month	
Non-Treated	6.4	1000 / 31.6	795±38 aDX[£]	742±55	91±17 aDX
		2000 / 63.2	974±29 bDX	920±40	97±02 aDX
		3000 / 94.7	1009±35 bDX	971±66	98±01 aDX
		4400 / 138.9	990±38 bDX	1000±38	98±01 aDX
	3.2	1000 / 31.6	779±22 aDX	757±24	39±12 aEX
		2000 / 63.2	933±42 bEX	898±25	48±08 abEX
		3000 / 94.7	994±21 cDEX	982±42	54±05 bEX
		4400 / 138.9	1035±18 dEX	1015±24	54±16 bEX
	1.6	1000 / 31.6	791±30 aDX	753±31	22±07 aFX
		2000 / 63.2	912±19 bEX	873±15	24±07 aFX
		3000 / 94.7	976±16 cEX	937±12	28±06 abFX
		4400 / 138.9	1027±22 dEX	1010±35	33±03 bFX
Steam Exploded	6.4	1000 / 31.6	849±47 aDY	847±75	82±18 aDX
		2000 / 63.2	1016±35 bDY	1023±53	97±01 bDX
		3000 / 94.7	1105±27 cDY	1121±41	98±02 bDX
		4400 / 138.9	1154±27 dDY	1179±29	100±00 bDY
	3.2	1000 / 31.6	846±41aDY	789±107	92±06 aDY
		2000 / 63.2	1059±25 bEY	1076±37	99±01 bDY
		3000 / 94.7	1126±33 cDY	1149±58	99±01 bDY
		4400 / 138.9	1165±26 dDY	1234±26	100±00 bDY
	1.6	1000 / 31.6	923±31 aEY	939±27	90±07 aDY
		2000 / 63.2	1070±20 bEY	1091±25	95±05 abDY
		3000 / 94.7	1123±16 cDY	1161±26	99±01 bDY
		4400 / 138.9	1163±24 dDY	1185±64	100±00 bDY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); § drop test was used to determine single pellet durability.

Table 6.3: Measured pellet density and durability data for non-treated and steam exploded oat straw at 10% moisture content (wb).

Oat Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Pellet Density (kg/m^3)		Durability (%)[§]
			After Pelleting	After One Month	
Non-Treated	6.4	1000 / 31.6	817±26 aDX[£]	771±46	89±08 aDX
		2000 / 63.2	945±24 bDX	918±54	99±01 bDX
		3000 / 94.7	982±29 cDX	968±41	99±01 bDX
		4400 / 138.9	985±43 cDX	966±19	99±01 bDX
	3.2	1000 / 31.6	811±26 aDX	791±34	52±05 aEX
		2000 / 63.2	907±24 bEX	915±45	64±08 bEX
		3000 / 94.7	948±24 cEX	982±47	75±13 cEX
		4400 / 138.9	988±35 dDX	986±29	82±11 cEX
	1.6	1000 / 31.6	795±23 aDX	800±34	44±08 aFX
		2000 / 63.2	912±17 bEX	865±29	45±09 aFX
		3000 / 94.7	992±26 cDX	1002±42	54±12 abFX
		4400 / 138.9	1024±26 dDX	995±48	57±10 bFX
Steam Exploded	6.4	1000 / 31.6	889±30 aDY	895±50	93±03 aDX
		2000 / 63.2	1034±55 bDY	1051±61	95±03 aDY
		3000 / 94.7	1130±32 cDY	1138±64	95±03 aDX
		4400 / 138.9	1151±21 cDY	1201±47	100±00 bDX
	3.2	1000 / 31.6	923±40 aEY	936±40	94±03 aDY
		2000 / 63.2	1068±17 bEY	1105±30	91±05 aDY
		3000 / 94.7	1129±30 cDY	1159±24	100±00 bEY
		4400 / 138.9	1144±14 cDY	1194±26	99±01 bDY
	1.6	1000 / 31.6	954±20 aFY	964±24	93±04 aDY
		2000 / 63.2	1090±16 bEY	1127±27	94±03 aDY
		3000 / 94.7	1143±16 cDY	1173±19	99±01 bEY
		4400 / 138.9	1165±27 dDY	1227±27	99±01 bDY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); § drop test was used to determine single pellet durability.

Table 6.4: Measured pellet density and durability data for non-treated and steam exploded wheat straw at 10% moisture content (wb).

Wheat Straw	Hammer Mill Screen Size (mm)	Applied Load (N) / Pressure (MPa)	Pellet Density (kg/m^3)		Durability (%)[§]
			After Pelleting	After One Month	
Non-Treated	6.4	1000 / 31.6	782±22 aDX[£]	760±50	97±04 aDX
		2000 / 63.2	923±32 bDX	983±24	95±05 aDX
		3000 / 94.7	965±52 cDX	1073±22	96±02 aDX
		4400 / 138.9	1001±21 dDX	1038±24	98±02 aDX
	3.2	1000 / 31.6	778±22 aDX	805±48	58±09 aEX
		2000 / 63.2	917±17 bDX	959±27	63±07 aEX
		3000 / 94.7	967±27 cDX	1047±31	64±08 aEX
		4400 / 138.9	1007±26 dDX	1042±48	64±08 aEX
	1.6	1000 / 31.6	819±23 aEX	815±30	63±07 aEX
		2000 / 63.2	948±18 bEX	941±37	52±09 bFX
		3000 / 94.7	997±19 cDX	999±27	56±06 abFX
		4400 / 138.9	1009±21 cDX	1022±18	57±07 abFX
Steam Exploded	6.4	1000 / 31.6	893±39 aDY	845±54	98±02 aDX
		2000 / 63.2	1064±26 bDEY	1033±38	98±02 aDX
		3000 / 94.7	1118±23 cDY	1153±34	99±01 aDX
		4400 / 138.9	1176±29 dDY	1159±26	100±00 aDX
	3.2	1000 / 31.6	909±37 aDY	895±49	97±02 aDY
		2000 / 63.2	1086±16 bDY	1093±18	98±02 abDY
		3000 / 94.7	1140±19 cDY	1144±31	98±02 abDY
		4400 / 138.9	1180±23 dDY	1132±47	100±00 bDY
	1.6	1000 / 31.6	926±47 aDY	896±49	96±02 aDY
		2000 / 63.2	1057±32 bEY	1057±41	95±05 aDY
		3000 / 94.7	1128±24 cDY	1100±30	96±04 aDY
		4400 / 138.9	1171±27 dDY	1118±51	94±04 aEY

‡10 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass and hammer mill screen size at various loads (a, b and c); same sample biomass and loads at various hammer mill screen sizes (D, E and F); for non-treated and steam exploded biomass at same hammer mill screen size (X and Y); § drop test was used to determine single pellet durability.

6.4.6 Single-Pellet Durability

At any specific hammer mill screen size, the durability of non-treated straw did not show any significant change with increase in applied pressures (Tables 6.1, 6.2, 6.3 and 6.4). However, durability of non-treated straw significantly decreased with a decrease in hammer mill screen size from 6.4 to 1.6 mm at any specific applied pressure. High durability values (>80%) were observed for non-treated straw grinds at 6.4 mm hammer mill screen size. This could be

primarily due to mechanical interlocking of relatively long fibers at higher grind sizes (Table 5.1).

High durability values (>80%) were obtained for steam exploded straw at any hammer mill screen size and applied pressure levels. Though lignin content of steam exploded straw was lower than non-treated straw, it is believed that the higher durability values are primarily due to higher cellulose content (Table 5.2). In addition, during the steam explosion process, the lignin and hemicelluloses are free from the lignocellulosic matrix, thus, are more available for binding the particles during compression (Figure 2.3 – Chapter 2).

The durability of non-treated and steam exploded straw at hammer mill screen size of 6.4 mm at any applied pressure was not significantly different. However, the durability of steam exploded straw pellets was significantly higher than non-treated straw at 3.2 and 1.6 mm hammer mill screen sizes at respective applied pressures. Statistically, no significant correlation (R^2 values) was obtained for change in density with applied pressure for any specific biomass and hammer mill screen sizes.

6.4.7 Pilot Scale Pelleting

The pellet mill produced pellets from ground non-treated barley, canola, oat and wheat straw at hammer mill screen sizes of 0.8 and 1.6 mm having moisture content of 17.5% (wb) and flax seed oil of 10% by weight. The non-treated ground straw at 3.2 and 6.4 mm screen size did not produce pellets. Similar pelleting process was followed for ground steam exploded straw. Due to very low bulk density and poor flowability, the steam exploded grinds did not produce pellets at any of the hammer mill screen sizes used in the investigation. However, the customized barley, canola, oat and wheat straw having 25% steam exploded material by weight at 0.8 mm screen size successfully produced pellets. Addition of higher percentage of steam exploded straw and customization at screen sizes of 1.6, 3.2, and 6.4 mm did not produce pellets, which could be due to the fact that adding steam exploded (having very low bulk density) to non-treated straw (having relatively higher bulk density) decreased the overall bulk density and flowability of the grinds, thus hindering the production of pellets. Shaw et al. (2007) reported similar trends where the quality of wheat straw pellets increased with an increase in moisture content to 15.9% (wb).

Figure 6.1 shows the photograph of pellets manufactured from barley, canola, oat and wheat straw from non-treated grinds at 0.8 and 1.6 mm screen sizes, and customized straw grinds at 0.8 mm having 25% steam exploded straw by weight.

Table 6.5 shows the pellet density obtained from non-treated straw samples at 1.6 and 0.8 mm, and customized sample having 25% steam exploded straw at 0.8 mm screen size. In general, pellet density increased with a decrease in screen size from 1.6 to 0.8 mm. However, no significant differences in density values were observed for non-treated samples at 0.8 mm and customized samples, except for canola and oat straw. This could be due to large fluctuation in individual pellet density values. All of the pellet density values reached near individual biomass particle densities at respective grind sizes (Table 5.1), except for barley straw pellets at 1.6 mm (1158±109 kg/m^3) and wheat straw pellets at 0.8 mm (1278±136 kg/m^3), which were higher. This could again be attributed to large fluctuations in individual pellet density values.

Bulk density of pellets from barley, canola, oat and wheat straw showed significant difference with grind size and customization, except for wheat straw pellets at 0.8 mm for non-treated and customized samples (Table 6.5). In general, average pellet bulk densities obtained for customized straw samples were higher (except for barley straw), which is consistent with increase in particle densities (Table 5.1). The bulk densities of pellets manufactured were higher than the minimum design value of 650 kg/m^{3}suggested by Obernberger and Thek (2004) for wood pellet producers, except for canola straw pellets from non-treated 1.6 mm (629±01 kg/m^3) and 0.8 mm customized (641±01 kg/m^3) samples, and non-treated oat straw at 1.6 mm (631±03 kg/m^3) screen size.

Table 6.5 also lists the durability values of pelletted samples. The durability of pellets obtained from non-treated straw samples at 1.6 and 0.8 mm, and customized sample having 25% steam exploded straw at 0.8 mm screen size were significantly different, except for oat straw at 1.6 mm and 0.8 mm customized samples. In general, higher durability values were observed for non-treated straw samples at 0.8 mm hammer mill screen size. The durability of pellets significantly increased with a decrease in grind size for non-treated samples from 1.6 to 0.8 mm. However, addition of steam exploded straw to non-treated straw at 0.8 mm screen size significantly decreased the durability, except for wheat straw. This could be due to the fact that steam exploded material has lower lignin content compared to non-treated straw (Table 5.2), which acts

as the natural binding agent. This observation is in contrast to Lam et al. (2008), who reported that the quality (durability) of pellets produced from steam exploded sawdust was 20% higher than non-treated sawdust. Though, it is important to note that high durability values (>80%) were obtained for all pilot scale pelleting tests.

Durability of pellets was negatively correlated to pellet mill throughput and was positively correlated to specific energy consumption (Table 6.5). The specific energy values obtained from pilot scale pellet mill are 10-25 times higher than reported by Mani et al. (2006b) for agricultural straw, using a single pellet Instron testing machine. The higher pellet mill specific energy numbers could be due to higher friction values and practical pelleting conditions, which are closer to industrial operations.

Lower bulk densities, and concerns with uneven and low flowability of straw grinds (especially, steam exploded straw grinds) are critical issues to be addressed in future to achieve a sustainable and broader pelleting process involving higher grind sizes. Therefore, pre-compression of straw grinds needs to be investigated as an alternative to increase their bulk density and flowability through the pellet mill (Larsson et al., 2008). In addition, steam conditioning of higher grind sizes should be explored that could result in production of pellets. However, an energy balance study is required to determine a trade-off between using steam conditioning or pre-compression vs. energy saved during hammer mill grinding of straw to large grind sizes.

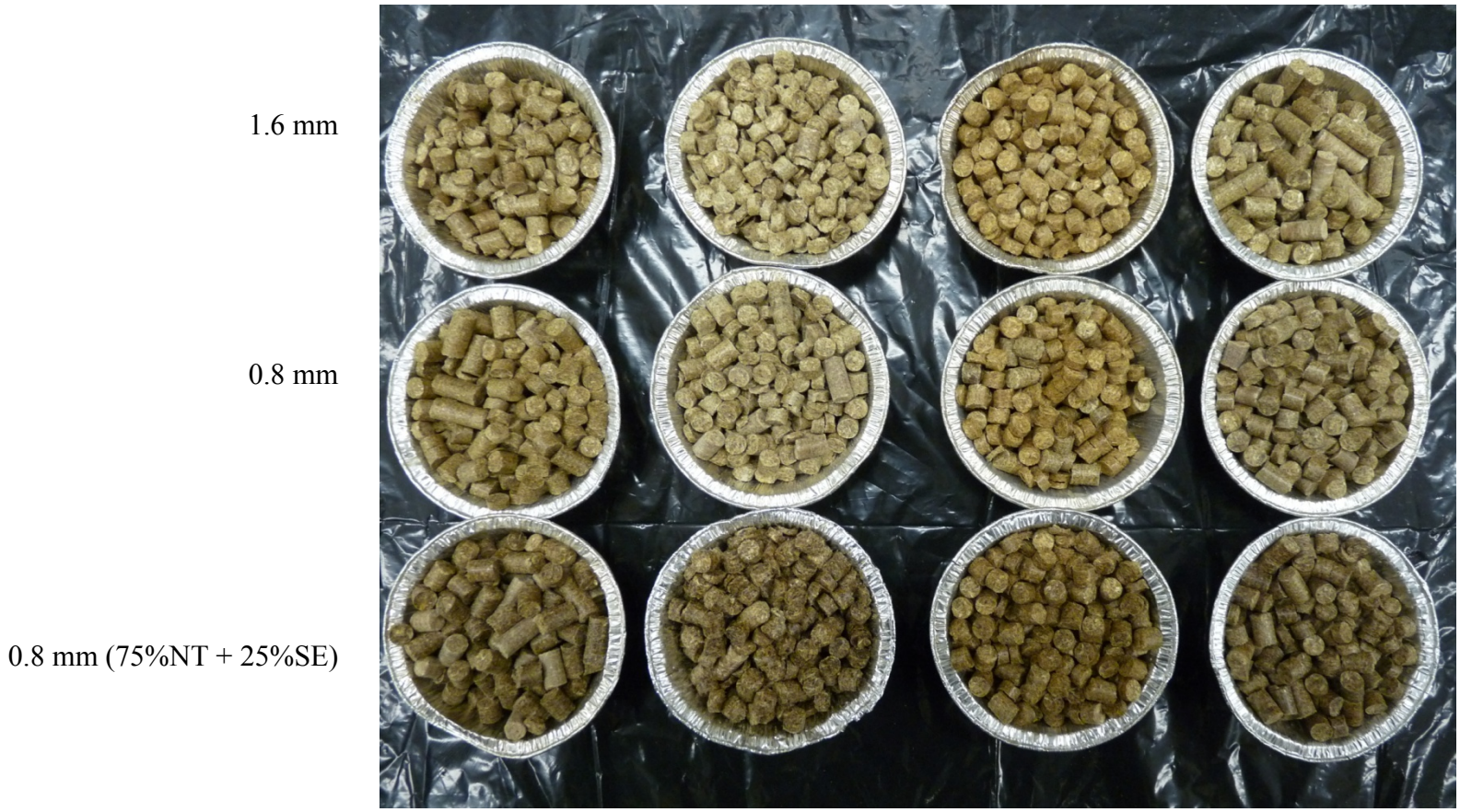


Figure 6.1: Photograph of pellets manufactured using a pilot scale pellet mill for non-treated (NT) straw at 1.6 and 0.8 mm hammer mill screen size, and customized grinds at 0.8 mm screen size having 25% steam exploded (SE) straw.

Table 6.5: Pellet density, durability, throughput and specific energy data for non-treated and steam exploded barley canola, oat and wheat straw at 17.5% moisture content (wb) and 10% flaxseed oil content.

Agricultural Biomass	Hammer Mill Screen Size (mm)	Pellet Density (kg/m^3)	Pellet Bulk Density (kg/m^3)	Durability (%)	Throughput (kg/h)	Specific Energy (MJ/t)
Barley Straw	1.6 (100% NT)	1158±109*†£ aD	665±01‡ aD	91±00‡ aD	4.88	293
	0.8 (100% NT)	1174±46 aD	700±07 bD	93±01 bD	4.21	353
	0.8 (75% NT + 25% SE)	1184±63 aD	714±02 cD	87±01 cD	3.46	301
Canola Straw	1.6 (100% NT)	1023±85 aE	629±01 aE	90±01 aD	3.86	385
	0.8 (100% NT)	1204±43 bDE	720±04 bE	95±00 bE	3.63	440
	0.8 (75% NT + 25% SE)	1144±50 cD	641±01 cE	82±00 cE	5.51	265
Oat Straw	1.6 (100% NT)	1140±63 abD	631±03 aE	89±01 aE	4.48	340
	0.8 (100% NT)	1188±78 aDE	649±02 bF	93±00 bD	3.81	344
	0.8 (75% NT + 25% SE)	1071±101 bE	676±06 cF	89±01 aF	4.03	335
Wheat Straw	1.6 (100% NT)	1163±57 aD	673±02 aF	94±01 aF	5.44	381
	0.8 (100% NT)	1278±136 bE	721±04 bE	95±01 bE	3.81	297
	0.8 (75% NT + 25% SE)	1213±88 abD	722±04 bG	95±00 cG	4.08	342

NT – Non-treated Straw Samples; SE – Steam Exploded Straw Samples; *10 replicates; ‡3 replicates; † 95% confidence interval; £ Student-Neuman-Keuls test at 5% level of significance for same sample biomass at various hammer mill screen sizes (a, b and c); at same hammer mill screen size for different sample biomass (D, E, F and G)

6.5 Conclusions

The following conclusions are derived from this study:

Single-Pelleting Test

1. Applied pressure and pre-treatment were significant factors affecting the pellet density.
2. Higher grind sizes and lower applied pressures resulted in higher relaxations (lower pellet densities) during storage of pellets.
3. Higher durability values (>80%) for non-treated straw at 6.4 mm hammer mill screen size and steam exploded straw at 6.4 to 1.6 mm hammer mill screen sizes were primarily due to mechanical interlocking of relatively long and free/ disintegrated fibers.

Pilot Scale Pelleting

1. Pellet bulk density and particle density are positively correlated.
2. Density and durability of agricultural straw pellets significantly increased with a decrease in hammer mill screen size from 1.6 mm to 0.8 mm.
3. Customization of agricultural straw by adding 25% of steam exploded straw by weight did not improve pellet quality.
4. Durability of pellets was negatively correlated to pellet mill throughput and was positively correlated to specific energy consumption.

Chapter 7

7. Factors Affecting Pellet Quality and Energy Analysis of Pelleting Process

A similar version of this chapter has been accepted for presentation at the CSBE/SCGAB Annual General Meeting. Only the energy analysis section of this paper has been presented in this Chapter since information on experimental design and data analysis has already been reported in Chapters 2, 4-6:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2011. A comprehensive analysis on the factors affecting densification of barley, canola, oat and wheat straw grinds. CSBE/SCGAB Annual General Meeting, Winnipeg, MB, Paper No. CSBE11-513, July 10-13: CSBE.

Contribution of Ph.D. Candidate

The current article builds on the experimental results and data analysis performed in Chapters 2, 4-6. This Chapter addresses the need to perform a study to further analyze the experimental data and identify factors that significantly contribute towards pellet quality. In addition, an overall energy balance to determine the feasibility of existing post-harvest processing and densification system in established. The data analysis and writing of article was performed by Phani Adapa in consultation with Dr. Lope Tabil and Dr. Greg Schoenau who also provided editorial input.

Contribution of this Paper to Overall Study

The objectives of this part of thesis are: 1) to determine the significance of major contributing factors (independent variables such as biomass type, treatment, pressure and grind size) on pellet density, durability and specific energy; and 2) to perform an overall energy analysis of the entire postharvest and densification process. The contributing factors towards pellet quality will guide a manufacturer to optimize most significant factors affecting pellet density, durability and specific energy required during manufacturing. An integrated approach to post-harvest processing and densification of non-treated and steam exploded straw was achieved, which resulted in the study of an overall energy balance of the densification system. This study is unique, since it is essential to see if there is a significant positive energy balance to the densification process enabling non-treated and steam exploded straw as suitable feedstock for biorefineries.

7.1 Abstract

Agricultural biomass residue such as barley, canola, oat and wheat straw has the potential to be used for sustainable production of bio-fuels and offset greenhouse gas emissions. The biomass substrate must be processed and handled in an efficient manner in order to reduce industry's operational cost as well as meet the requirement of raw material for biofuel production. Biomass has low bulk density, making it difficult and costly to store and transport in its native loose form. Therefore, in this study, an integrated approach to densification of non-treated and steam exploded barley, canola, oat and wheat straw was developed. During this process the significance of major contributing factors (independent variables such as biomass type, treatment, pressure and grind size) on pellet density, durability and specific energy were determined. It has been found that the applied pressure (60.4%) was the most significant factor affecting pellet density followed by the application of steam explosion pre-treatment (39.4%) for lab-scale single pelleting experiments. Similarly, the type of biomass (47.1%) is the most significant factor affecting durability followed by the application of pre-treatment (38.2%) and grind size (14.6%) for pellets manufacture from pilot-scale pellet mill. Also, the applied pressure (58.3%) was the most significant factor affecting specific energy required to

manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar effect affect on specific energy for lab-scale single pelleting experiments. Overall energy analysis of post-harvest processing and densification of agricultural straw was performed, which showed that a significant portion of original agricultural biomass energy (89-94%) is available for the production of biofuels. Almost, similar amount of specific energy is required to produce pellets from barley, canola, oat and wheat straw grinds. Customized pellets having steam exploded straw required more energy to manufacture resulting in availability of only 89% of total energy for biofuel production.

7.2 Introduction

7.2.1 The Need for Densification

Agricultural biomass residues have the potential for the sustainable production of bio-fuels and to offset greenhouse gas emissions (Campbell et al., 2002; Sokhansanj et al., 2006). Straw from crop production and agricultural residues existing in the waste streams from commercial crop processing plants have little inherent value and have traditionally constituted a disposal problem. In fact, these residues represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass (Liu et al., 2005). New methodologies need to be developed to process the biomass making it suitable feedstock for bio-fuel production. In addition, some of the barriers to the economic use of agricultural crop residue are the variable quality of the residue, the cost of collection, and problems in transportation and storage (Bowyer and Stockmann, 2001; Sokhansanj et al., 2006).

Compaction of low bulk density agricultural biomass is a critical and desirable operation for sustainable and economic availability of feedstock for biofuel industry. Due to its high moisture content, irregular shape and size, and low bulk density, biomass is very difficult to handle, transport, store, and utilize in its original form (Sokhansanj et al., 2005). Densification of biomass into durable compacts is an effective solution to these problems and it can reduce material waste. Densification can increase the bulk density of biomass from an initial bulk density of 40-200 kg/m^3 to a final compact density of 600-1200 kg/m^3 (Adapa et al., 2007; Holley, 1983; Mani et al., 2003; McMullen et al., 2005; Obernberger and Thek, 2004). Because

of their uniform shape and size, densified products can easily be handled using existing handling and storage system used for cereal grains. They can be easily adopted in direct-combustion or co-firing with coal, gasification, pyrolysis, and utilized in other biomass-based conversions (Kaliyan and Morey, 2006a) such as biochemical processes.

7.2.2 Fuel Pellet Quality and Contributing Factors

The quality of fuel pellet is usually assessed based on its density and durability. High density of pellet represents higher energy per unit volume of material, while durability is the resistance of pellets to withstand shear and impact forces applied during handling and transportation. High bulk density increases storage and transport capacity of pellets. Since feeding of boilers and gasifiers generally is volume-dependent, variations in bulk density should be avoided (Larsson et al., 2008). A bulk density of 650 kg/m^3 is stated as design value for wood pellet producers (Obernberger and Thek, 2004). Low durability of pellets results in problems like disturbance within pellet feeding systems, dust emissions, and an increased risk of fire and explosions during pellet handling and storage (Temmerman et al., 2006).

7.2.2.1 Effect of Moisture Content on Pellet Quality

The moisture in biomass both acts as a facilitator of natural binding agents and a lubricant (Kaliyan and Morey, 2006a). Many studies have indicated that the production of high quality pellets is possible only if the moisture content of the feed is between 8 and 12% (wb). Moisture contents above or below this range would lead to lower quality pellets (Hill and Pulkinen, 1988; Kashaninejad et al., 2011; Li and Liu, 2000; Obernberger and Thek, 2004; Shaw and Tabil, 2007). In general, an increase in moisture content from 10 to 44% could result in up to 30-40% decrease in pellet densities of biomass (Chancellor, 1962; Grover and Mishra, 1996; Gustafson and Kjelgaard, 1963; Kaliyan and Morey, 2006a; Mani et al., 2002 and 2006b; Smith et al., 1977). However, the percentage decrease in density depends on the type of biomass. Therefore, a moisture content of 10% (w.b.) is considered as optimal moisture content to obtain high density and durability pellets.

7.2.2.2 Effect of Grind Size on Pellet Quality

Pre-processing operations such as particle size reduction / grinding is critical in order to increase the surface area of lignocellulosic biomass prior to densification (Mani et al. 2004). Particle size

reduction increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process (Drzymala, 1993).

7.2.2.3 Steam Explosion Pre-treatment of Biomass

Upon densification, many agricultural biomass materials, especially those from straw and stover, result in a poorly formed pellets or compacts caused by lack of understanding on the natural binding characteristics and interaction of the components that make up biomass during compaction. These pellet are more often dusty, difficult to handle and costly to manufacture. The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al. 2005). It is postulated that by disrupting the lignocellulosic matrix of biomass materials via application of various chemical, physico-chemical (steam explosion, microwave, and radio frequency heating), and biological pre-treatment, the compression and compaction characteristics can be improved (Shaw 2008; Kashaninejad and Tabil, 2011).

Steam explosion: Steam explosion is one of the most applied pre-treatment processes owing to its low use of chemicals and limited energy consumption (Harmsen et al., 2010). Steam explosion results in the hemicelluloses being hydrolyzed and become water soluble, the cellulose is slightly depolymerized, and the lignin melts and is depolymerized, which aid in binding particles together during densification. Zandersons et al. (2004) stated that activation of lignin and changes in the cellulosic structure during the steam explosion process facilitate the formation of new chemical bonds. Lam et al. (2008) reported that the quality (durability) of compacts produced from steam exploded sawdust was 20% higher than non-treated sawdust.

During steam explosion pre-treatment process, the lignocellulosic biomass is heated with high pressure saturated steam having temperatures typically in the range of 180-230^{o}C for 2-10 minutes. Subsequently, the substrate is quickly flashed to atmospheric pressure resulting in the rapid vaporization and expansion of the water inside the biomass (Grous et al., 1985; Kokta and Ahmed, 1998; Zimbardi et al., 1999). This causes great reduction in the particle size of the substrate (Fig. 2.3; Chapter 2). The heart of the explosion pulping process is the reactor, which allows the use of high pressure during heating and cooking. The reactor can be of either the batch

(Fig. 7.1) (Jin and Chen, 2006) or continuous type (Fig. 3.1; Chapter 3) (Kokta and Ahmed, 1998; Chapter 3).

The extent of chemical and structural modifications from steam-explosion pre-treatment depends on residence time, temperature, particle size and moisture content (Sun and Cheng, 2002). However, the severity (Ro) of steam explosion is quantified as a function of retention time and reaction temperature (Eq. 7.1) (Overend and Chornet, 1987; Viola et al., 2008).

$$\mathrm{Ro} = \mathrm{t} \times \exp\left(\frac{\mathrm{T}-100}{14.75}\right) \tag{7.1}$$

Where *T* is the temperature in ^{o}C and *t* is the time in minutes.

According to Zimbardi et al. (1999), the simplest way to carry out steam explosion is by batch procedure, hence widely reported in literature. However, the continuous reactors are of major interest for industrial applications. Ideally, the results of batch steam explosion process should be similar to continuous process. However, it has been observed that even though the products are obtained at the same treatment, severity in batch and continuous reactors are macroscopically different at first sight. Consequently, Zimbardi et al. (1999) have developed experimental relationship between the two systems useful in making the data transfer straightforward (Equation 7.2).

$$log(Ro)_{Batch} = 1.50 \times (log(Ro)_{Continuous} - 1) \tag{7.2}$$

In addition, studies have been carried out to try to improve the results of steam explosion by addition of chemicals such as acid or alkali (Cara et al., 2008; Harmsen et al., 2010; Stenberg et al., 1998; Zimbardi et al., 2007). Limitations of steam explosion include the formation of degradation products that may inhibit downstream processes (Garcia-Aparicio et al., 2006).

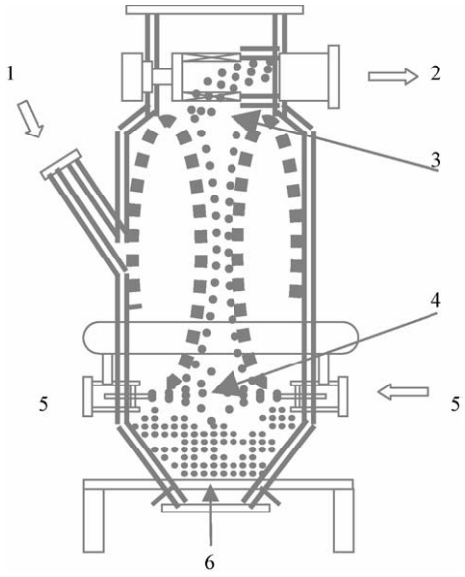


Figure 7.1: Schematic diagram of the FJM-200 fluidized bed opposed jet mill. 1, Infeed; 2, collection; 3, classification section; 4, grinding section; 5, compressed air; 6, discharge opening (Jin and Chen, 2006).

7.2.3 Specific Energy Consumption during Pelleting

An overall specific energy analysis is desired in order to understand the net amount of energy available for the production of biofuels after postharvest processing and densification of agricultural straw. Consequently, various energy intensive steps involved in pelleting of agricultural biomass are shown in the flow process diagram in Figure 7.2.

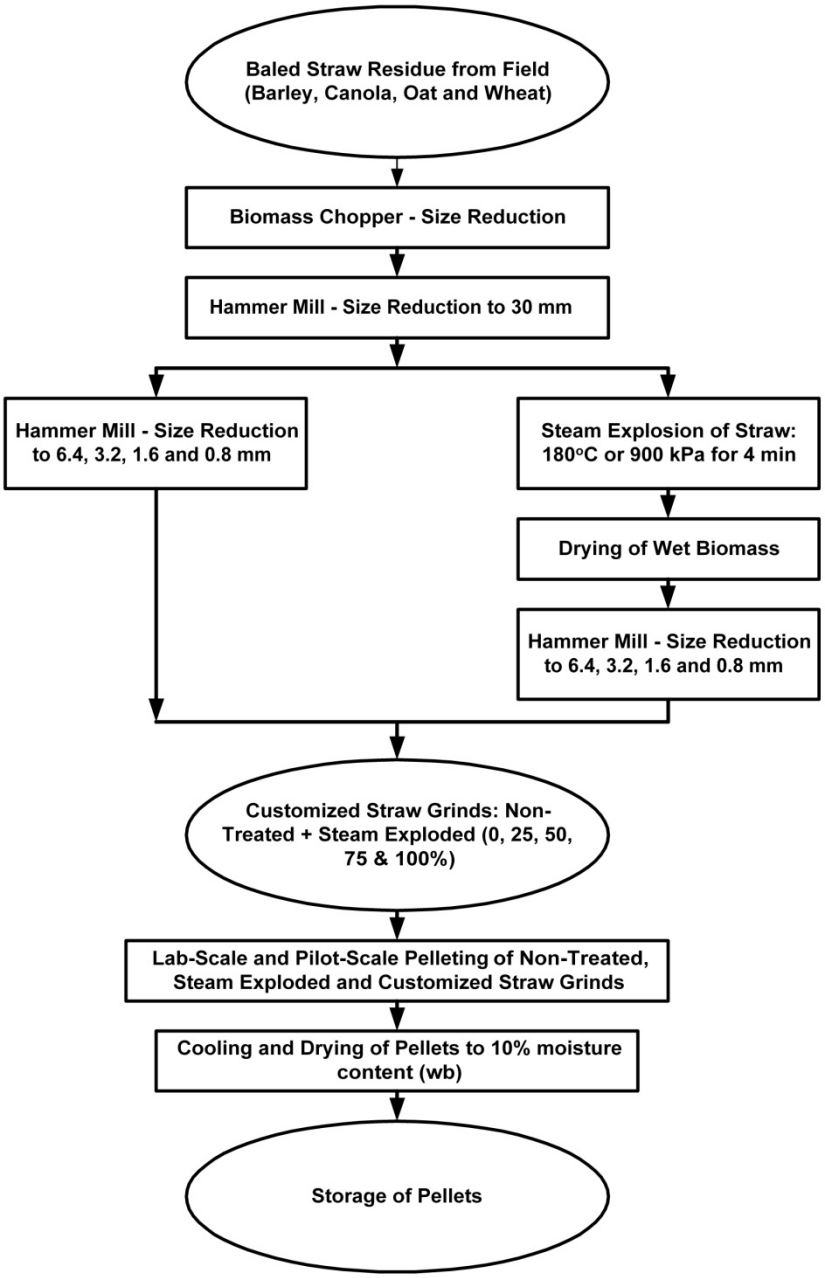


Figure 7.2: Flow chart showing the energy intensive steps involved in pelleting of agricultural biomass

7.2.3.1 Chopping

Baled agricultural biomass from the field does not have good flowing characteristics and may not flow easily into grinders such as hammer mills and disc refiners. Therefore, the biomass needs to be chopped with a chopper (rotary shear shredder) / knife mill / tub grinder to accommodate bulk

flow and uniformity of feed rate. A chopper, knife cutter, or knife mill is often used for coarse size reduction (>50 mm) of stalk, straw, and grass feed stocks (Bitra et al., 2009). Knife mills reportedly worked successfully for shredding forages under various crop and machine conditions (Cadoche and López, 1989).

Bitra et al. (2009) reported that the total specific energy (including energy to operate the knife mill) for agricultural biomass chopping increases with knife mill speed. The total specific energy for knife mill and tub grinder has been observed to have negative correlation with screen size and mass feed rate (Arthur et al., 1982; Bitra et al., 2009; Himmel et al., 1985). They reported that the total specific energy requirement of a tub grinder decreased from 2696 to 1181 MJ/t with an increase in screen size from 12.7 to 50.8 for rectangular wheat straw bales. The grinding rate (throughput) increased from 0.137 to 0.267 t/min with an increase in screen size from 12.7 to 50.8 (Arthur et al., 1982).

For tub grinders, an increase in screen size from 19.1 mm to 127.0 mm results in an increase in geometric mean length of particles and throughput, but a decrease in bulk density from 207 to 69 kg/m^3 of the particles and specific energy consumption from 804 to 68 MJ/t (Kaliyan et al., 2010).

7.2.3.2 Hammer Mill Grinding

Size reduction is an important energy intensive unit operation essential for bioenergy conversion process and densification to reduce transportation costs (Bitra et al., 2009; Soucek et al., 2003). Energy consumption of grinding biomass depends on initial particle size, moisture content, material properties, feed rate of the material and machine variables (Lopo, 2002).

Typically, hammer mills are used in forage processing industry as they are relatively inexpensive, easy to operate and produces wide range of particles (Lopo, 2002). Hammer mills have achieved merit because of their ability to finely grind a greater variety of materials than any other machines (Scholten et al., 1985). The performance of a hammer mill is measured in terms of energy consumption and geometric mean diameter and particle size distribution of the ground product (Mani et al., 2004). They have concluded that among the four materials (wheat and barley straw, corn stover and switchgrass) studied at two moisture levels and three grind sizes,

switchgrass had the highest specific energy consumption of 27.6 kWh/t, and corn stover had the lowest specific energy consumption of 11.0 kWh/t at 3.2 mm screen size (Mani et al., 2004).

Screen Size: Hammer mill screen opening size was the most significant factor affecting mill performance (Fang et al., 1997) and also has significant effect on mean particle size (Pfost and Headley, 1971). The specific energy required to grind agricultural biomass significantly increases with a decrease in hammer mill screen size and shows a negative power correlation (Arthur et al., 1982; Soucek et al., 2003). Similarly, a negative correlation between specific energy and particle size of biomass as affected by hammer mill screen sizes was observed in Chapter 2. However, two other studies reported a second-order polynomial relationship between the specific energy requirements for grinding biomass (Mani et al. 2004; Sitkei, 1986). Usually, the mean geometric particle size for any particular biomass decreases with a decrease in hammer mill screen size (Chapter 2). It has been reported that wider particle size distribution is suitable for compaction (pelleting / briquetting) process (Mani et al., 2004). During compaction, smaller (fine) particles rearrange and fill in the void space of larger (coarse) particles producing denser and durable compacts (Tabil, 1996).

Operating Speed (Peripheral Velocity): The speed has a significant effect on mean particle size (Pfost and Headley, 1971). The total specific energy of hammer mill grinding has direct correlation to an increase in hammer tip speed (Bitra et al., 2009; Vigneault et al., 1992). High speed hammer mills with smaller diameter rotors are good for fine or hard-to-grind material. However, at high tip speeds, material moves around the mill parallel to the screen surface making the openings only partially effective. At slower speeds, the material impinges on the screen at a greater angle causing greater amounts of coarser feed to pass through (Balk, 1964).

Hammer Angles and Thickness: The direct energy input for grinding also depends on hammer angles. In general, the specific energy for grinding decreases with an increase in hammer degrees (Bitra et al., 2009). In addition, the specific energy for grinding increases with an increase in hammer thickness (Vigneault et al., 1992).

Material Moisture Content and Feed Rate: A positive correlation has been reported between moisture content and specific energy consumption for grinding of agricultural biomass (Balk, 1964; Mani et al., 2004; Soucek et al., 2003). Feeding rate also has significant effect on specific

energy consumption during hammer mill grinding and has positive correlation (O'Dogherty, 1982).

Bulk and Particle Densities, and Geometric Mean Particle Size: Usually, the bulk and particle density of agricultural straw significantly increases with a decrease in hammer mill screen size (Chapter 2). The geometric mean particle size of pre-treated straw is usually smaller than that of the non-treated straw. This could be due to the fact that application of pre-treatment disrupts/ disintegrates the lignocellulosic structure of the biomass (Sokhansanj et al., 2005) leading to lower shear strength (easier to grind the straw).

7.2.3.3 Steam Explosion Pre-treatment

Energy required during steam explosion process can be calculated by following the procedure described in Abolins and Gravitis (2009). A model provided in Figure 7.3 is used to calculate the cost of steam explosion treatment in terms of energy. The effect can be assessed by some critical limit of moisture content M_c at which the energy spent on heating the waterless part of the biomass to the required temperature is equal to the energy spent on raising the temperature of the moisture (Eq. 7.3).

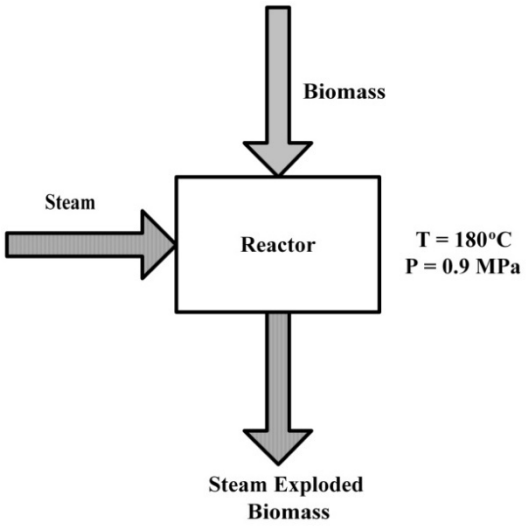


Figure 7.3: Block diagram of steam explosion model used for energy calculations

$$M_c = \frac{C_b(\Delta T)}{C_b(\Delta T)+(\Delta h)m_w} \tag{7.3}$$

Where,

C_b - specific heat of dry biomass, kJ/kg ^oC;

ΔT - difference between the operation temperature and the initial temperature, ^oC;

Δh - enthalpy difference of water content of the biomass with respect to ΔT, kJ/kg; and

m_w - mass of moisture in biomass, kg.

Energy E_b consumed to heat the biomass up to the required operation temperature can be calculated as follows (Equation 7.4) (Abolins and Gravitis, 2009).

$$E_b = C_b(\Delta T) + m_w(\Delta h) \tag{7.4}$$

Similarly, the energy for biomass treatment by steam explosion being supplied by saturated steam at the operation temperature can be expressed in terms of the amount of steam consumed per unit mass of the processed dry organic substance. Assuming that biomass is heated at the expense of energy released at the condensation of saturated steam at the operation temperature, the mass of condensed saturated steam m_{cs} is found from the following equation (7.5) (Abolins and Gravitis, 2009):

$$m_{cs}E_{evap} = E_b \tag{7.5}$$

Where,

E_{evap} - is the heat of evaporation at the operating temperature, kJ/kg; and

E_b - is given by equation (7.4)

The total amount of saturated steam necessary for the process is found as the sum of the amount of steam being condensed to heat the biomass and the amount of steam m_o necessary to maintain the pressure in the reactor (Equation 7.6) (Abolins and Gravitis, 2009):

$$m_o = \frac{V}{v} \tag{7.6}$$

Where,

V - volume of the reactor occupied by the biomass containing one mass unit of the dry substance to be treated, m^3;

ν - the specific volume of saturated steam under operation pressure and temperature, m^3/kg.

Therefore, the energy to generate the total amount of steam $m_s = m_{cs} + m_o$ is provided in equation (7.7) (Abolins and Gravitis, 2009):

$$E_s = m_s(\Delta h) \tag{7.7}$$

Where,

E_s - total energy required to generate steam, kJ/kg.

Total amount of energy required during steam explosion process is given by the following equation (7.8):

$$E_t = E_b + E_s \tag{7.8}$$

7.2.3.4 Drying of Wet Biomass

During the steam explosion process, the moisture content of biomass significantly increases and reaches to approximately 80% (wb). Consequently, the wet biomass must be dried to approximately 12% (wb) prior to storing and densification into pellets. Therefore, the energy supplied to evaporate water depends upon the drying temperature. The quantity of energy required per kg of water is called the latent heat of vaporization. The heat energy required to vaporize water under any given set of conditions can be calculated from the latent heats given in the steam table (Earle, 1983) and provided by the following equation (7.9):

$$\begin{aligned} &Heat\ energy\ (kJ)\ required\ for\ 1\ kg\ biomass \\ &\quad = heat\ energy\ to\ raise\ temperature\ of\ biomass\ to\ drying\ temperature \\ &\quad + latent\ heat\ to\ remove\ water \end{aligned} \tag{7.9}$$

Where,

$Heat\ energy = C_b(\Delta T)$

C_b - specific heat of biomass, kJ/kg ^oC; and

ΔT - temperature change, ^oC.

$Latent\ heat = m_w L$

m_w - mass of water, kg; and

L - latent heat of vaporization of water, kJ/kg.

7.2.3.5 Lab-Scale Pelleting: Specific Energy for Compaction and Extrusion of a Pellet

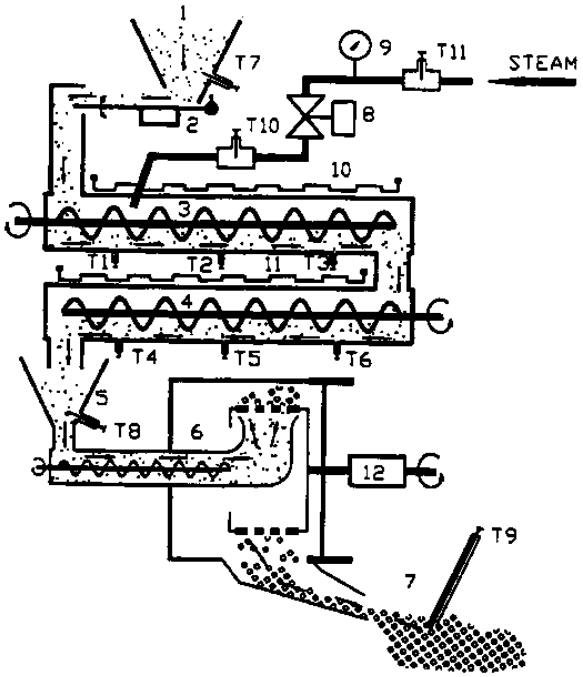
During the compression and extrusion processes of individual biomass compacts, the force-displacement data is recorded and can be used to calculate the specific compression and extrusion energies following the methodology reported by Adapa et al. (2006) and Mani et al. (2006). The area under the force-displacement curve can be integrated using the trapezoid rule (Cheney and Kincaid, 1980); when combined with the pellet mass, the specific energy values in MJ/t can be calculated.

During single-pellet compression and extrusion, the pellets are prepared by densifying material against a base plate (representing the specific energy required to overcome friction within the straw grinds) as opposed to commercial operation where compacts are formed due to back-pressure effect in the die. Therefore, the specific energy required to extrude the compact should be included, which will closely emulate the specific energy required to overcome the friction between the ground compressed biomass and the die. Mani et al. (2006) have indicated that the extrusion (frictional) energy required to overcome the skin friction was roughly half of the total energy (12-30 MJ/t) for corn stover. Mewes (1959) showed that roughly 40% of the total applied energy was used to compress the materials (straw and hay) and the remaining 60% was used to overcome friction. Faborode and O'Callaghan (1987) studied the energy requirement for compression of fibrous agricultural materials. They reported that chopped barley straw at 8.3% (wb) moisture content consumed 28-31 MJ/t of energy, while un-chopped material consumed 18-27 MJ/t. Shaw (2008) reported that between 95 and 99% of the total specific energy was required to compress the grinds, whereas between 1 and 5% of the total specific energy was

required to extrude the compact in single compact tests. Shaw (2008) also reported that the mean values of specific compression energy ranged from 7.2 (pretreated wheat straw using steam explosion) to 39.1 MJ/t (wheat straw).

7.2.3.6 Pilot-Scale Pelleting

Pilot-scale densification of biomass is required to demonstrate the feasibility of production of pellets by application of various variables studied during single-pellet experiments. A pilot-scale pellet mill such as CPM CL-5 pellet mill (Fig. 7.4) (California Pellet Mill Co., Crawfordsville, IN) can be used for processing of agricultural straw grinds into pellets. The pellet mill usually consists of a corrugated roller and ring die assembly, which compacts and extrudes the biomass grinds from the inside of a ring-shaped die by pressure applied by rolls where either the die or the roll suspension is rotating. The pellet mill energy consumption (kWh) should be recorded in real time using a data logger connected to a computer and should be used to calculate the specific energy (MJ/t) required to manufacture pellets from ground agricultural biomass.



Thermocouples: T1 to T11

1. Feed Hopper
2. Vibrating Tray
3. Paddle Conveyor
4. Paddle Conveyor
5. Feed Hopper to Pellet Mill
6. Screw Conveyor
7. Pellet Collection Bucket
8. Steam Control Valve
9. Steam Pressure Gauge
10. Double Chamber Steam Chest
11. Double Chamber Steam Chest
12. V-belt Drive for Pellet Mill

Figure 7.4: Schematic diagram of CPM CL-5 pellet mill (Adapa et al., 2004).

7.2.3.7 Cooling of Pellets

Biomass pellets are cooled to reduce the moisture and temperature in the pellets to levels that are safe for storage and easy to handle. The relatively high levels of moisture (soft pellets) and temperature (~100^{o}C) in the pellets arise from the frictional heating of the die during pelleting. Inadequate cooling and drying of pellets contributes to poor pellet quality, spoilage, heating and spontaneous combustion, caking in storage bags and holding bins (Biomassenergy, 2011; Fasina, 1994). Thus, it is a common practice to let them get air cooled through a conveyor belt. Under these conditions, the lignin polymer inside biomass fibres gets stabilized, producing pellets of increased hardness properties (Biomassenergy, 2011).

Typically, pellets experience a temperature change greater than 70^{o}C during the cooling process. The energy required to cool the pellets (sensible energy) is three times greater than the energy required to dry the pellets (latent heat) (Fasina, 1994). Fasina and Sokhansanj (1993) reported that the sensible heat for cooling alfalfa pellets was 2600 MJ/h assuming an average specific heat of 1800 J/kg.K and the pelleting plant operates at capacity of 16 t/h. The latent heat was 800 MJ/h when the latent heat of vaporization of alfalfa pellets was taken to be 2500 kJ/kg (Fasina and Sokhansanj, 1993).

Hence, there is a need to perform a study to analyze the experimental data and identify factors that significantly contribute towards pellet quality. The results of analysis will guide a manufacturer to optimize most significant factors affecting pellet density, durability and specific energy required during manufacturing. In addition, an overall energy analysis by identifying energy needs at various steps indicated in Figure 7.4 should be performed to make an assessment of energy that will be available for production of biofuel and optimize the post-harvest processing path in the flowchart. Therefore, the objectives of this part of the study are:

1. to determine the significance of major contributing factors (independent variables such as biomass type, treatment, pressure and grind size) on pellet density, durability and specific energy; and
2. to perform an overall energy analysis of post-harvest processing and densification of agricultural straw.

7.3 Materials and Method

The materials and method for this Chapter are similar to what has been reported in Chapters 2, 4-6. The method for measuring specific energy for chopping, grinding, steam explosion, pelletizing and pellet cooling is outlines as below:

7.3.1 Chopper and Hammer Mill

During the chopping and grinding experiments, 3 kg each of either non-treated or steam exploded straw was manually fed into the chopper (Fig. 2.1; Chapter 2) (no screen) and hammer mill (Fig. 2.2) having four screen sizes of 30, 6.4, 3.2 and 1.6 mm. The power drawn by the chopper and hammer mill motors, and the time required for the grinding process were measured and recorded. The power required to run empty chopper and hammer mill were recorded prior to the introduction of material in order to obtain base line data. This allowed determining the net power required to grind the material. The specific energy (kWh t^{-1}) required for chopping and grinding was determined by integrating the area under the power demand curve for the total time required to grind the sample for pre-determined quantity of material (Mani et al., 2004). Each test was performed in replicates of three.

Total specific energy required to grind non-treated straw can be obtained by adding specific energy required for chopping of the baled straw plus the specific energy required for hammer mill grinding.

Total specific energy required to grind steam exploded straw to 6.4, 3.2 and 1.6 mm hammer mill screen size can be obtained by adding specific energy required for chopping of the baled straw, specific energy for hammer mill grinding of straw at a screen size of 30 mm, and respective specific energy required for hammer mill grinding of steam exploded material at 6.4, 3.2 and 1.6 mm.

7.3.2 Steam Explosion

The steam explosion of ground straw obtained using 30 mm hammer mill screen size was performed at the pilot-scale continuous steam explosion plant of FPInnovations, Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized disc refiner having a plate gap

of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive set to operate at 33.3 Hz. The biomass flow through the refiner is wet (in suspension). The throughput of the equipment can vary between 50 and 200 kg of dried material per hour, depending on the bulk density of the raw material and the desired final particle size of the steam exploded material. The feed rate of agricultural straw into the digester was controlled using a plug screw feeder. The digester was operated at 180^{o}C (steam pressure of 900 kPa) for 4 min to perform steam explosion of the agricultural biomass. A flash tube convective dryer having 90 m long tube was used to dry the steam exploded barley, canola, oat and wheat straw at an average moisture content of 70.1%, 80.7%, 76.7%, and 81.0% (wb) to approximately an average moisture content of 12.2, 13.6, 12.0 and 12.0% (wb), respectively. The direct heating of air was performed using 1172 kW natural gas burner, which has variable control to operate at different temperatures.

The specific energy required during steam explosion process and drying of wet steam exploded biomass was performed by following the procedure described in sections 7.2.3.3 and 7.2.3.4, respectively.

7.3.3 Lab-Scale Single Pelleting

The compaction apparatus was used to make a single compact in one stroke of the plunger from ground straw samples. In order to simulate frictional heating during commercial pelleting operation, the compaction die was maintained at a temperature of 95±1^{o}C (Adapa et al., 2006 and Mani et al., 2006b). The mass of samples used for making compacts varied between 0.5 and 0.7 g. Compressive force was applied using the Instron Model 1011 testing machine fitted with a 5000 N load cell and a 6.25 mm diameter plunger. Four preset loads of 1000, 2000, 3000 and 4400 N corresponding to pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were used to compress samples in the die. The crosshead speed of the Instron testing machine was set at 50 mm/min. After compression, the plunger was retained in place for 30 s once the preset load was attained in order to avoid spring-back effect of biomass grinds (Adapa et al., 2006 and Mani et al., 2006b). Later, the base plate was removed and the compact was ejected out of the die by using the plunger. The mass, length and diameter of compacts were measured to determine the density in kg/m^{3}, following the extrusion of the compact. Ten replicates (pellets) were made using each ground straw samples.

During compression and extrusion process of individual compacts, the force-displacement data were recorded. Specific compression and extrusion energies were calculated following the methodology of Mani et al. (2006a). The area under the force-displacement curve was integrated using the trapezoid rule (Cheney and Kincaid, 1980); when combined with the pellet mass, it yielded the specific energy values in MJ/t. The specific energy calculations did not include the energy required to operate the Instron testing machine.

7.3.4 Pilot Scale Pelleting

A laboratory scale CPM CL−5 pellet mill (California Pellet Mill Co., Crawfordsville, IN) was used for processing of non-treated and steam exploded agricultural straw grinds into pellets. The pellet mill consisted of a corrugated roller (diameter 85.0 mm) and ring die assembly. The ring die size (radius) and length (thickness) were 125.3 and 44.6 mm, respectively. The ring hole diameter and l/d ratio were 6.10 mm and 7.31, respectively. The rotational speed of the pellet mill was 250 rpm. All of the above specifications were adopted from previous studies performed by Tabil and Sokhansanj (1996), Adapa et al. (2004), and Hill and Pulkinen (1988) to produce high quality pellets from biomass.

At the onset of pelleting experiments, 2 kg each of ground non-treated barley, canola, oat and wheat straw grinds from 6.4, 3.2, and 1.6 mm hammer mill screen size were re-moistened to 10% moisture content (wb) by adding/ sprinkling a calculated amount of water and mixed a rotating concrete mixer. Only one moisture level of 10% (wb) was used based upon literature review to produce high density and quality pellets/briquettes from various straw and biomass (Kaliyan and Morey, 2006a and 2007; Mani et al., 2006a; Obernberger and Thek, 2004; Shaw and Tabil, 2007; Stevens, 1987). Due to low bulk density and poor flowability of ground straw, the pellet mill continuously clogged without producing any pellets. The non-treated and steam exploded straw was ground using 0.8 mm hammer mill screen size to improve the flowability of straw grinds. As pre-compaction (Larsson et al., 2008) and steam addition (Thomas et al., 1997) are energy intensive operations, it was decided to add both moisture and flax seed oil in incremental steps of 0.5% to further increase the bulk density and flowability of ground straw through pellet mill. Addition of moisture and oil to a level of 17.5% and 10%, respectively, resulted in production of pellets. Similar process was repeated for customized ground straw obtained from 6.4, 3.2, 1.6, and 0.8 mm hammer mill screen sizes.

The feed rate of material to the pellet mill was controlled using a vibratory feeder. Each successful pilot scale pelleting test was performed for an average period of 10 min. During this period, manufactured pellets were collected and weighed to determine the pellet mill throughput (kg/h). In addition, the pellet mill energy consumption (kWh) was recorded in real time using a data logger connected to a computer and was used to calculate the specific energy (MJ/t) required to manufacture pellets from respective agricultural biomass. The manufactured pellets were allowed to dry in ambient condition for 24 hr and subsequently stored in black plastic bags for at least 2 weeks prior to pellet density and durability tests.

7.3.5 Cooling of Pellets

The cooling of pellets would be done using ambient air. The only energy required would be to power the fans, which would be small compared to the other operating energies and was therefore, excluded from the calculations.

7.3.6 Statistical Analysis

The experiments were set up as completely randomized experimental design with 10 replications of compacts and four-variable (straw, pre-treatment (steam explosion), hammer mill screen size and pressure) factorial design. Density, durability and specific energy were the dependent variables, while straw, pre-treatment, hammer mill screen size and pressure were the independent variables. Statistical analyses were conducted using SAS for Windows (version 8.2) (SAS Institute, 1999). In order to further understand and explain the experimental variables and their interactions, the SAS general linear model (GLM) was used. Values of sum of squares (SS) for each factor (independent variable) were obtained from the GLM factorial model. Subsequently, the SS were re-calculated to percentage base and presented in graphical form (Head et al., 2010).

7.4 Results and Discussion

7.4.1 Contribution of Factors Effecting Pellet Quality

The experimental data, regression analysis and discussion on properties of ground biomass (geometric mean particle diameter, bulk density, and particle density), lignocellulosic

composition, pellet density, pellet durability and specific energy are provided in Chapters 5 and 6. The present section will focus on contribution of independent variables such as biomass, pre-treatment, applied pressure and grind size on pellet density, durability and specific energy.

After performing the statistical analysis on density data for pellets manufactured from lab-scale single pelleting experiments as shown in Tables 5.3-5.6 (Chapter 5), it was determined that the applied pressure (60.4%) was the most significant factor affecting pellet density followed by the application of steam explosion pre-treatment (39.4%) (Fig. 7.5). Type of biomass and grind size did not have significant effect on the pellet density (Fig. 7.5).

Similarly, the statistical analysis on durability data for pellets manufactured from pilot-scale pelleting experiments as shown in Tables 6.5 (Chapter 6) indicated that the type of biomass (47.1%) is the most significant factor affecting durability followed by the application of pre-treatment (38.2%) and grind size (14.6%) (Fig. 7.6).

The statistical analysis of specific energy data for pellets manufactured from lab-scale single pelleting experiments as shown in Tables 5.3-5.6 (Chapter 5) showed that the applied pressure (58.3%) was the most significant factor affecting specific energy required to manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar effect affect on specific energy (Fig. 7.7).

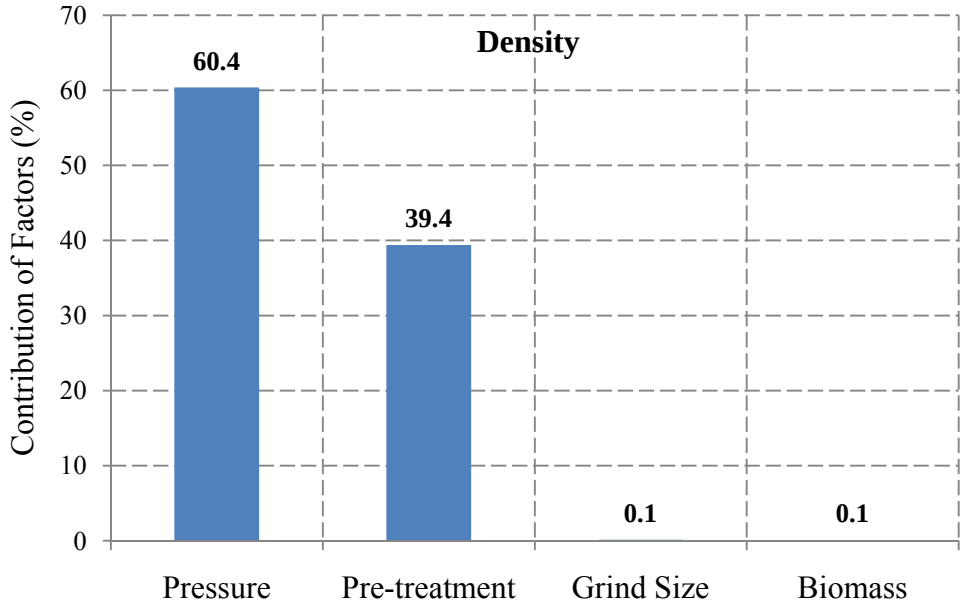


Figure 7.5: Contribution of independent variables to density of pellets manufactured from lab-scale single pelleting experiments (Chapter 5)

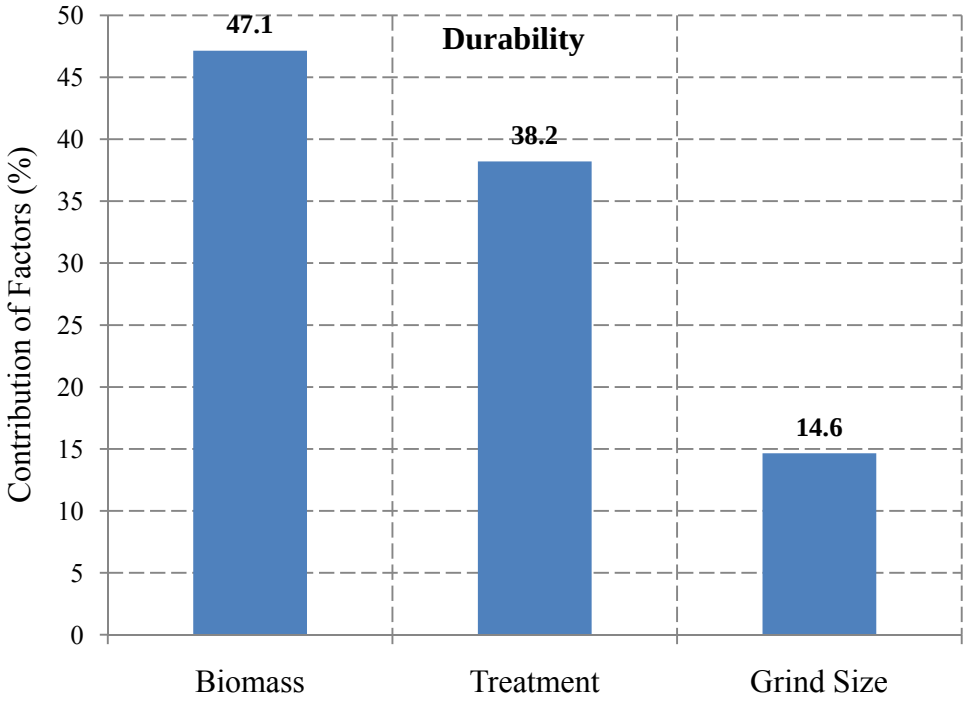


Figure 7.6: Contribution of independent variables to durability of pellets manufactured from pilot-scale pelleting experiments (Chapter 6)

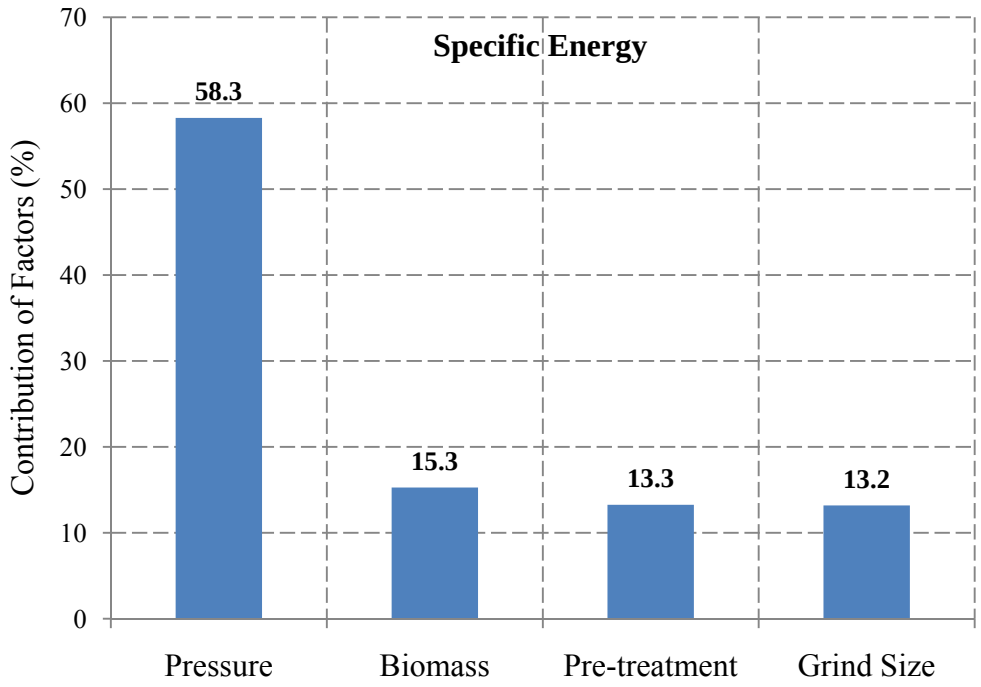


Figure 7.7: Contribution of independent variables to specific energy of pellets manufactured from lab-scale single pelleting experiments (Chapter 5)

7.4.2 Overall Energy Analysis

An overall specific energy analysis is desired in order to understand the net amount of energy available for the production of biofuels after postharvest processing and densification of agricultural straw (Fig. 7.4). Barley, canola, oat and wheat straw at moisture content of 13.5, 15.1, 13.1 and 15.6% (wb), respectively was subjected to steam explosion pre-treatment at 180^{o}C (steam pressure of 900 kPa) for 4 min. Table 7.1 shows the thermodynamic characteristics of saturated steam and biomass along with specific energy calculations. Subsequently, the steam exploded barley, canola, oat and wheat straw at an average moisture content of 70.1, 80.7, 76.7 and 81.0% (wb) to approximately an average moisture content of 12.2, 13.6, 12.0 and 12.0% (wb), respectively. The specific energy calculations for drying wet steam exploded biomass are provided in Table 7.2.

Table 7.1: Thermodynamic properties of saturated steam and biomass, and energy analysis.

Thermodynamic Property	Steam	Barley	Canola	Oat	Wheat
Enthalpy Difference Δh at 180°C, kJ/kg	2777				
Evaporation Energy E_{evap} at 180°C, kJ/kg	2014				
Specific Volume v at 180°C, m^3/kg	0.194				
Mass of Moisture Content m_w (Equation 7.3), kg		0.677	0.594	0.701	0.572
Straw Specific Heat C_b (Anh et al., 2009), kJ/kg.°C		1.63[a]	1.57[a]	1.57	1.63
Energy to Heat the Biomass E_b (Equation 7.4), kJ/kg		312.2	298.5	301.3	309.3
Mass of Condensed Steam m_{cs} (Equation 7.5), kg		0.155	0.148	0.150	0.154
Volume of Reactor V, m^3 (5 liters)[b]	0.005				
Amount of Steam m_o (Equation 7.6), kg		0.026	0.026	0.026	0.026
Total Steam $m_s = m_{cs} + m_o$, kg		0.181	0.174	0.175	0.179
Energy to Generate Total Steam E_s (Equation 7.7), kJ/kg		502.1	483.2	487.1	498.1
Total Energy for Steam Explosion E_t (Equation 7.8), kJ/kg		814.3	781.7	788.4	807.4

[a] The bulk density reported by Anh et al. (2009) for wheat straw was comparable to barley straw and for oat straw was comparable to canola straw hence similar straw specific heat values

[b] Assuming that 1 kg of biomass would fit loosely with an volume of 5 liters (Abolins and Gravitis, 2009)

Table 7.2: Specific energy required to dry wet steam exploded biomass.

Properties and Calculations	Barley	Canola	Oat	Wheat
Biomass Initial Moisture Content, % (wb)	70.1	80.7	76.7	81.0
Biomass Final Moisture Content, % (wb)	12.2	13.6	12.0	12.0
Dryer Inlet Temperature 120°C				
Latent Heat of Vaporization for water at 120°C is 2202 kJ/kg[a]				
Initial Mass of Water in 1 kg of Biomass	0.701	0.807	0.767	0.810
Mass of Dry Biomass, kg	0.299	0.193	0.233	0.190
Final Mass of Water, kg	0.042	0.030	0.032	0.026
Mass of Water Evaporated, kg	0.659	0.777	0.735	0.784
Specific heat of Biomass, kJ/kg°C	1.63	1.57	1.57	1.63

Temperature of Biomass at Reactor Outlet is 100°C (assumption)				
Energy Required to Raise Biomass Temperature to 120°C, kJ	32.6	31.4	31.4	32.6
Latent Energy Required to Remove Water, kJ	1452.1	1710.1	1619.0	1726.6
Total Energy Required for Drying, kJ	1484.7	1741.5	1650.4	1759.2
Specific Energy Required for Drying, kJ/kg	2251.4	2242.4	2244.7	2243.6

[a] Latent heat is obtained from steam table provided by Earle (1983)

The overall specific energy analysis was performed for pilot-scale pelleting of non-treated and customized (75% non-treated + 25% steam exploded) barley, canola, oat and wheat straw at 1.6 and 0.8 mm hammer mill screen sizes (Table 7.3). The specific energy for grinding of straw at 0.8 mm was calculated using regression equations reported in Chapter 2. The specific energy for chopping and grinding of biomass, production of pellets using pellet mill and higher heating values for straw were obtained from experimental data (Chapters 2 and 6, and Table 7.3). In addition, the energy required for operating the chopper, hammer mill and pellet mill were 337, 759 and 429 W, respectively.

On average, the operation of biomass chopper required five times more energy than chopping of biomass. Contrarily, the grinding of biomass required on an average three times more energy than operation of hammer mill. Interestingly, almost same amount of energy was required to operate the pellet mill and production of pellets.

Total specific energy required to form pellets increased with a decrease in hammer mill screen size from 1.6 to 0.8 mm and also the total specific energy significantly increased with customization of straw at 0.8 mm screen size (Table 7.3). Figures 7.8-7.11 shows the contribution of factors toward total specific energy required to manufacture barley, canola, oat and wheat straw pellets. In all of the plots, pellet mill consumes the highest proportion of total specific energy followed by hammer mill and chopper for non-treated barley straw at 1.6 mm grind size. A decrease in grind size to 0.8 mm for non-treated straw significantly increases the proportion of hammer mill contribution. The most significant factor for customized straw is the specific energy required for steam explosion pre-treatment (including drying) followed by pellet mill (Fig. 7.8-7.11). It has been observed that the net specific energy available for production of

biofuel is a significant portion of original agricultural biomass energy (89-94%) for all agricultural biomass (Table 7.3). Almost, similar amount of specific energy is required to produce pellets from barley, canola, oat and wheat straw grinds. Customized pellets having steam exploded straw required more energy to manufacture resulting in availability of only 89% of total energy for biofuel production. It should be noted that the specific energy required for operating the steam explosion, drying and cooling units are not included in the total numbers. In future studies, an increase in the higher heating values due to addition of flax seed oil to agricultural straw should also be include.

Table 7.3: Overall specific energy showing the net energy available for production of biofuels after postharvest processing and densification of agricultural straw.

Treatment	Hammer Mill Screen Size (mm)	Specific Energy (MJ/t)							HHV (MJ/t)	Net Energy [γ] (MJ/t)
		Chopping Biomass	Grinding Biomass	Steam Explosion	Drying of Steam Exploded Biomass	Pilot-Scale Pelleting	Total Operating Energy[¥]	Total[§£]		
Barley										
NT*	1.6	11.3	90.4			293	528.8	924	16400	15476
NT	0.8	11.3	206.6			353	528.8	1100	16400	15300
75% NT + 25% SE*	0.8	11.3	189.3	203.6	562.9	301	528.8	1797	16650	14853
Canola										
NT	1.6	7.1	128.5			385	466.8	987	16700	15713
NT	0.8	7.1	363.3			440	466.8	1277	16700	15423
75% NT + 25% SE	0.8	7.1	341.6	195.4	560.6	265	466.8	1837	17100	15263
Oat										
NT	1.6	9.9	149.5			340	529.6	1029	16400	15371
NT	0.8	9.9	253.6			344	529.6	1137	16400	15263
75% NT + 25% SE	0.8	9.9	245.2	197.1	561.2	335	529.6	1878	16750	14872
Wheat										
NT	1.6	8.2	153.3			381	505.6	1048	17000	15952
NT	0.8	8.2	382.7			297	505.6	1194	17000	15806
75% NT + 25% SE	0.8	8.2	332.1	201.9	560.9	342	505.6	1951	17200	15249

*NT – Non-Treated; SE – Steam Exploded;

¥ Total Operating Energy is the no load energy required for operating the chopper, hammer mill, and pellet mill; energy required for operating the chopper, hammer mill and pellet mill were 337, 759 and 429 W, respectively;

§ Energy is based on moisture contents of the biomass at operating conditions (refer to Chapters 2, 5-6) and not based on dry matter;

£ Total Specific Energy = Specific Energy (Chopping Biomass + Grinding Biomass + Steam Explosion + Pilot-Scale Pelleting + Operating Energy); and

γNet Energy = HHV – Total

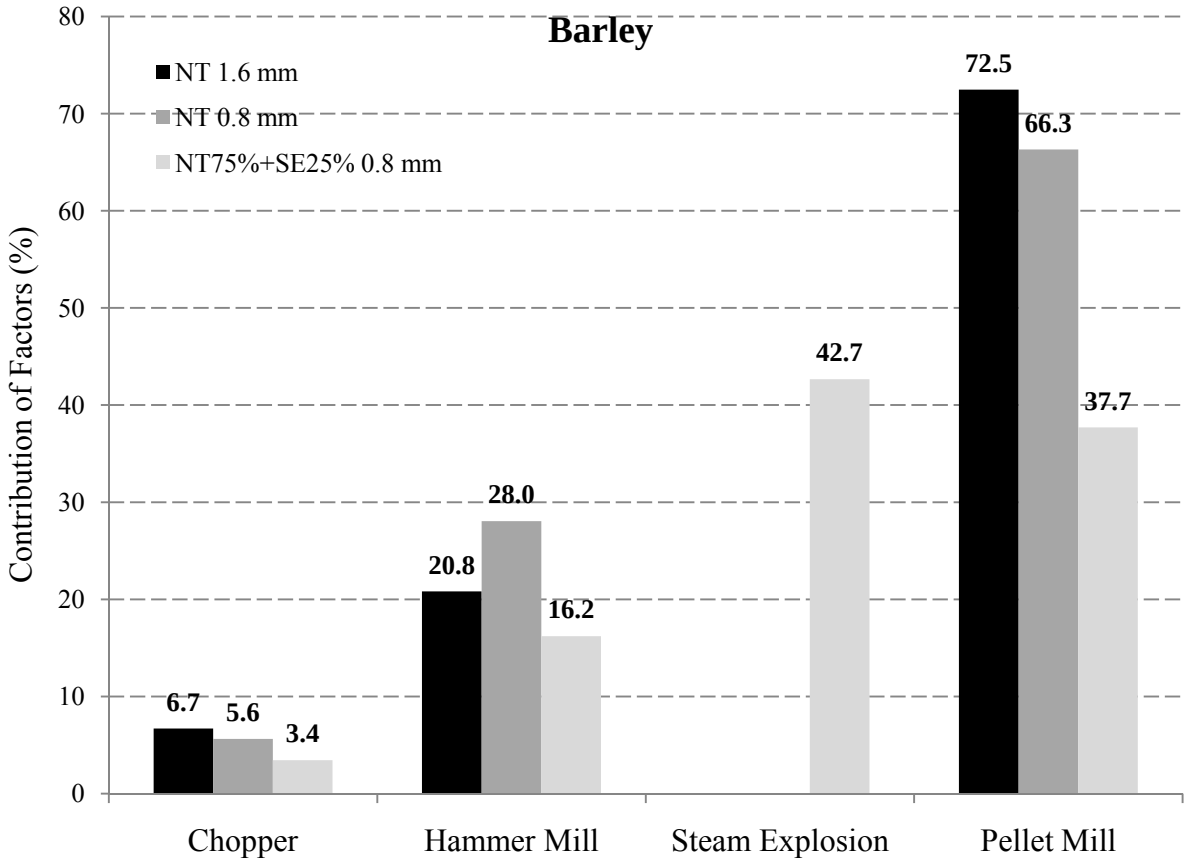


Figure 7.8: Contribution of factors toward total specific energy required to manufacture barley straw pellets

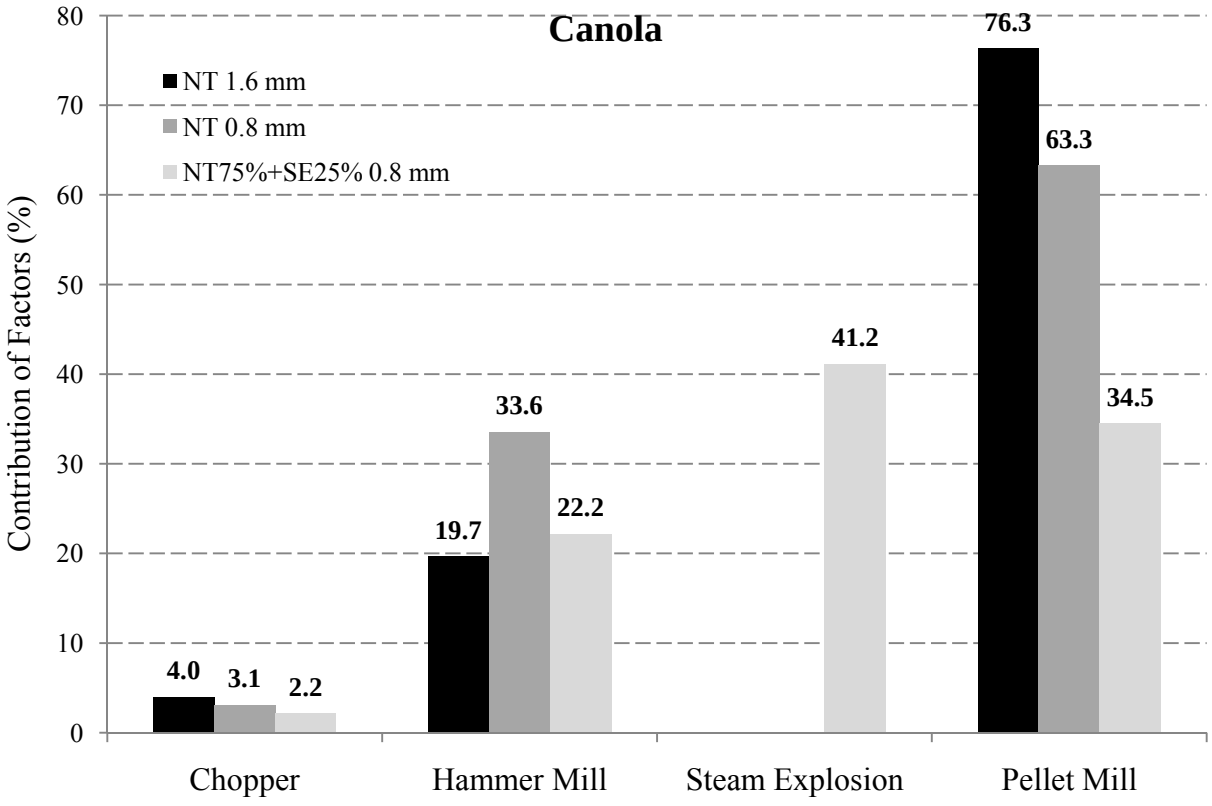


Figure 7.9: Contribution of factors toward total specific energy required to manufacture canola straw pellets

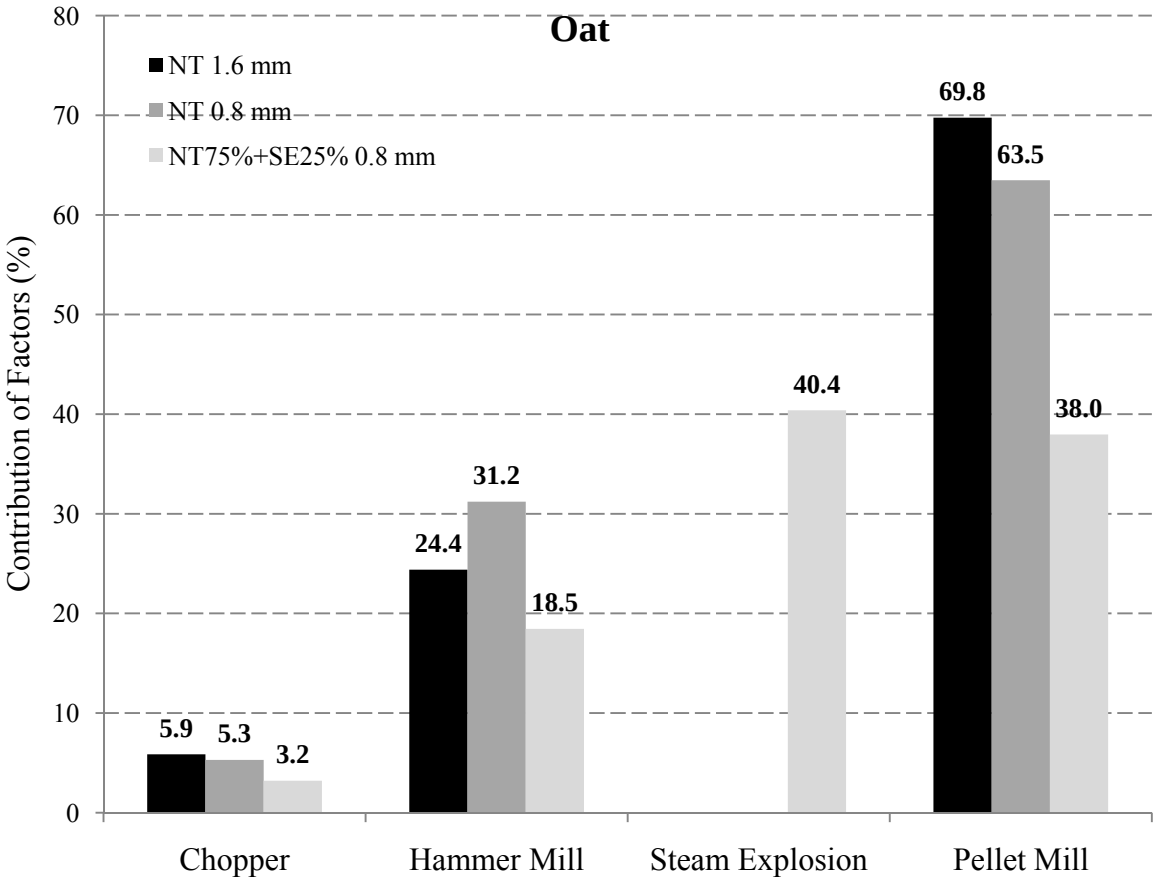


Figure 7.10: Contribution of factors toward total specific energy required to manufacture oat straw pellets

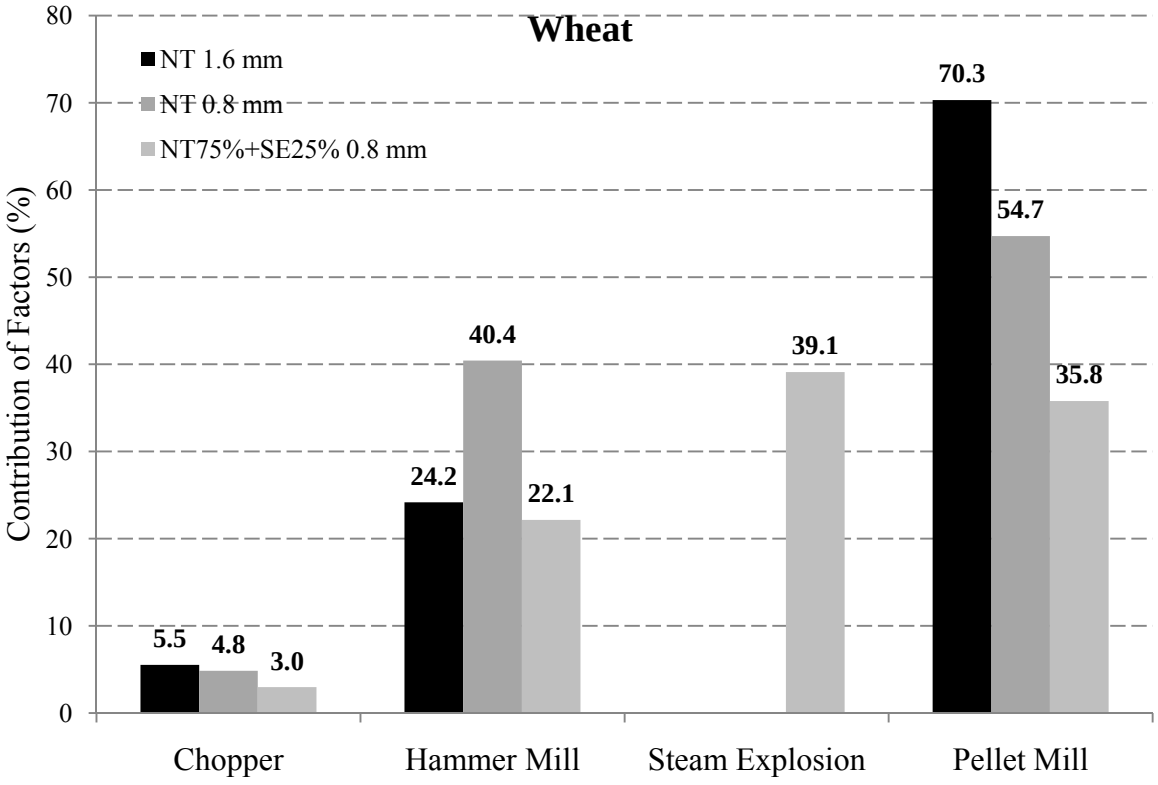


Figure 7.11: Contribution of factors toward total specific energy required to manufacture wheat straw pellets

7.5 Conclusions

From this analysis it is concluded that the applied pressure (60.4%) was the most significant factor affecting pellet density followed by the application of steam explosion pre-treatment (39.4%) for lab-scale single pellet experiments. Similarly, the type of biomass (47.1%) is the most significant factor affecting durability followed by the application of pre-treatment (38.2%) and grind size (14.6%) for pellets manufacture from pilot-scale pellet mill. Also, the applied pressure (58.3%) was the most significant factor affecting specific energy required to manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar effect affect on specific energy for lab-scale single pellet experiments.

The pellet mill consumed the highest proportion of total specific energy followed by hammer mill, cooler and chopper for non-treated barley straw at 1.6 mm grind size. A decrease in grind size to 0.8 mm for non-treated straw significantly increases the proportion of hammer mill contribution. The most significant factor for customized straw is the specific energy required for steam explosion pre-treatment followed by pellet mill. An overall energy balance showed that a significant portion of original agricultural biomass energy (89-94%) is available for the production of biofuels. Almost, similar amount of specific energy is required to produce pellets from barley, canola, oat and wheat straw grinds. Therefore, biofuel pellet manufacturers should focus on increasing the pellet bulk density and durability since comparable amount of specific energy is required at any specific grind size and pretreatment. Also, it is recommended to develop or use pellet mills that could pellet agricultural straw grinds obtained from higher hammer mill screen sizes (>1.6 mm) to increase the net available specific energy for production of biofuels.

Chapter 8

8. General Discussion

8.1 Overall Ph.D. Project Discussion

This Ph.D. thesis explored the effects of steam explosion pre-treatment and pre-processing (size reduction) techniques on densification of barley, canola, oat and wheat straw residue resulting in high quality (density and durability) pellets. It has been determined that an increase in bulk density of biomass also increases the net calorific content per unit volume of pellets, and facilitates easy and economical storage, transport and handling of the biomass. Pre-treatment and pre-processing methods disintegrate the basic lignocellulosic structure of biomass, and change the relative composition of lignin, cellulose and hemicelluloses in the material. The application of pre-treatments breaks the long-chain hydrogen bond in cellulose, making hemicelluloses amorphous, and loosening the lignin out of the lignocellulosic matrix, resulting in better quality (physically) pellets. During this process, the high molecular amorphous polysaccharides are reduced to low molecular components to become more cohesive in the presence of moisture during the densification process. In addition, physical and frictional properties of agricultural straw are significantly altered, which has direct significance on designing new and modifying existing bins, hoppers and feeders for handling and storage of straw for biofuel industry. As a result, regression equations were developed to enhance process efficiency by eliminating the need for experimental procedure while designing and manufacturing of new handling equipment.

Particle size reduction increases the total surface area, pore size of the material and the number of contact points for inter-particle bonding in the compaction process. However, particle size reduction demands significant amount of energy resulting in higher processing costs. Therefore, it is essential to develop predictive regression equations that could be used by biorefineries to perform economic feasibility of establishing a processing plant. In addition, the measurement of

particle size distribution and test of normality was performed to determine whether the ground agricultural biomass has the potential to produce high quality pellets.

Rapid characterization and quantitative analysis of cellulose-hemicellulose-lignin composition of agricultural biomass is required prior to and after application of various pre-processing and pre-treatment methods. Traditionally, chemical analyses of the individual components (e.g., lignin) of lignocellulosics have been performed by acid hydrolysis followed by gravimetric determination of lignin. These methods can provide highly precise data. However, these methods are laborious, time-consuming, and, consequently, expensive to perform and sample throughput is limited. Through literature review, it has been shown that the Fourier Transform Infrared Spectroscopy (FTIR) can be used to rapidly characterize and quantify lignocellulosic composition of agricultural biomass. Therefore, a novel process to quantify the lignocellulosic composition of agricultural biomass using FTIR was developed and verified using data from traditional lab-based experiments. Subsequently, regression equations were developed to predict the lignocellulosic content of agricultural biomass using pure cellulose, hemicelluloses and lignin as reference samples. It is envisioned that the new procedure will bring unique perspective to the post-harvest processing of biomass and will enhance process efficiency and bring economic benefits to the manufacturer.

Densification of biomass into durable compacts is an effective solution to meet the requirement of raw material for biofuel production. The compression characteristics of ground agricultural biomass vary under various applied pressures. It is important to understand the fundamental mechanism of the biomass compression process, which is required to design an energy efficient compaction equipment to mitigate the cost of production and enhance the quality of the product. To a great extent, the strength of manufactured compacts depends on the physical forces that bond the particles together. These physical forces are generated in three different forms during compaction operations: a) thermal; b) mechanical; and c) atomic forces. To customize and manufacture high quality products that can withstand various forces during transportation and handling, it is essential to predict desirable and dependent quality parameters (density and durability) with respect to various independent variables (pre-treatment, grind size, applied pressure, hold time, die temperature, and moisture content). In addition, specific energy

requirements of manufacturing biomass pellets should be established, which can assist in determining the economic viability of densification process.

Due to high moisture content, irregular shape and size, and low bulk density, biomass is very difficult to handle, transport, store, and utilize in its original form. Densification of biomass into durable compacts is an effective solution to these problems and it can reduce material waste. In addition, high density is often associated with high durability of pellets. The density of biomass pellet has been observed to significantly increase with an increase in applied pressure and a decrease in hammer mill screen size. Application of pre-treatment has observed to significantly increase the pellet density since pre-treated straw has lower geometric particle diameters and significantly higher particle densities. Statistically, agricultural biomass did not have any significant effect on pellet density, while steam explosion pre-treatment, applied pressure, and hammer mill screen size had significant effect. It has been concluded that the applied pressure (60.4%) was the most significant factor effecting pellet density followed by the application of steam explosion pre-treatment (39.4%) for lab-scale single pelleting experiments.

Agricultural biomass, steam explosion pre-treatment, applied pressure, and hammer mill screen size all had significant effect on pellet durability from lab-scale single pelleting experiment. In general, durability of pellets increased with an increase in applied pressure and grind size, and application of pre-treatment. The type of biomass (47.1%) is the most significant factor affecting durability followed by the application of pre-treatment (38.2%) and grind size (14.6%) for pilot-scale pelleting experiments. Also, it has been observed that density and durability of pellets were positively correlated (Table 6.5; Chapter 6).

The quality (density and durability) of pellets obtained from lab-scale tests can also be correlated to the particle size distribution and test of normality performed in Chapter 2. The analysis concludes that irrespective of particle size distribution, the density of pellet is dictated by the applied pressure. However, at constant pressure, the density of pellets will be higher at lower grind sizes. Contrarily, the durability of pellet is significantly affected by the particle size distribution, which is higher at higher grind sizes. This is primarily due to interlocking of fibrous structure of material in addition to particle-particle binding.

Pellets are formed by subjecting the biomass grinds to high pressures, wherein the particles are forced to agglomerate. During this process, significant amount of energy is required to compact the biomass grinds to facilitate particle-particle binding. Specific energy required to form a pellet has been significantly affected by the type of agricultural biomass, steam explosion pre-treatment, applied pressure and hammer mill screen size. The applied pressure (58.3%) was the most significant factor effecting specific energy required to manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar affect on specific energy for lab-scale single pelleting experiments. The total and compression specific energy for compaction of non-treated and steam exploded barley, canola, oat and wheat straw at any particular hammer mill screen size significantly increased with an increase in applied pressure and significantly decreased with a decrease in hammer mill screen size.

Pilot-scale pelleting of barley, canola, oat and wheat straw was performed in order to determine the feasibility of effectively densifying the agricultural biomass and build on the results and conclusions derived from lab-scale pelleting. In addition, customization of grounds straw material was also performed by adding steam exploded biomass in increments of 25% to non-treated ground straw for respective biomass at specific grind size. Pilot-scale pelleting has posed different set of practical concerns, primarily associated with lower bulk density and poor flowability of ground straw through pellet mill, which continuously clogged without producing any pellets. Therefore, the moisture level was increased and oil was added to the ground straw in order to pelletize the material. Even then the pellets were only formed at lower hammer mill grind sizes. Similar observation was made to customized straw having 25% steam exploded straw where pellets were produced only at lower grind sizes. Addition of higher percentage of steam exploded straw and customization of straw at higher screen sizes did not produce pellets, which could be due to the fact that adding steam exploded (having very low bulk density) to non-treated straw (having relatively higher bulk density) decreased the overall bulk density and flowability of the grinds, thus hindering the production of pellets. Interestingly, the density of pellets produced from customized straw did not show any significant difference from non-treated straw, while durability of customized straw decreased. These results do not completely agree with lab-based tests (compression and compaction analysis) in Chapter 5, where density and durability of steam exploded straw was significantly higher than non-treated straw. This warrants the need to design new pilot-scale pelleting technology and development of new

procedure since existing technology seems to over-work on the low bulk density straw and results in clogging of pellet mill. In addition, the pilot-scale pellet mill is also limited in terms of motor power to take in widely diverse bulk density raw materials. However, this may not be true in commercial mills which are driven by huge motors with powers of 250 to 400 hp (convert to kW). Lower bulk densities, and concerns with uneven and low flowability of straw grinds (especially, steam exploded straw grinds) are critical issues to be addressed in future to achieve a sustainable and broader pelleting process involving higher grind sizes. Therefore, pre-compression of straw grinds needs to be investigated as an alternative to increase their bulk density and flowability through the pellet mill, which is now an integral part of some newer pellet mills.

However, on a positive note, all of the pilot-scale pelleting experiments produce high durability pellets and the bulk densities of pellets manufactured were higher than the minimum design value of 650 kg/m^3. Durability of pellets was negatively correlated to pellet mill throughput and was positively correlated to specific energy consumption.

An overall energy balance showed that a significant portion of original agricultural biomass energy (89-94%) is available for the production of biofuels. Almost, similar amount of specific energy is required to produce pellets from barley, canola, oat and wheat straw grinds. Therefore, biofuel pellet manufacturers should focus on increasing the pellet bulk density and durability since comparable amount of specific energy is required at any specific grind size and pretreatment. Customized pellets having steam exploded straw required more energy to manufacture resulting in availability of only 89% of total energy for biofuel production. Also, it is recommended to develop or use pellet mills that could pellet agricultural straw grinds obtained from higher hammer mill screen sizes (>1.6 mm) to increase the net available specific energy for production of biofuels.

8.2 Achievement of Research Objectives

All of the research objectives listed in Chapter 1 (Section 1.7) have been achieved over the course of the Ph.D. project. These are listed from 1 to 7 as in Section 1.7 to indicate which

objective has been attained. The thesis chapters in which the thesis objectives are achieved are included in brackets after each numbered listing for reference.

1. to determine and establish relationships of geometric mean particle size with specific energy requirements, bulk and particle densities, and perform a comparative analysis for grinding non-treated and steam exploded barley, canola, oat and wheat straws; (Chapter 2)

2. to determine the effect of steam explosion pretreatment, hammer mill screen size, and normal forces on coefficient of internal friction and cohesion properties of non-treated and steam exploded barley, canola, oat and wheat straw; (Chapter 3)

3. to estimate critical parameters in analytical specification of lignocellulosic biomass and consequently, to develop and validate a rapid method for the qualitative and quantitative analysis of cellulose-hemicellulose-lignin composition of non-treated and steam exploded barley, canola, oat and wheat straw using Fourier Transform Infrared Spectroscopy (FTIR); (Chapter 4)

4. to determine the effect of pressure and biomass grind size on density and specific energy requirements for compacting non-treated and steam exploded barley, canola, oat and wheat straw grinds; (Chapter 5)

5. to determine the pressure-volume and pressure-density relationship to analyze the compression characteristics of non-treated and steam exploded barley, canola, oat and wheat straw using three compression models, namely: Jones (1960), Cooper-Eaton (1962), and Kawakita-Ludde (1971), models; (Chapter 5)

6. to produce high density and high durability pellets from ground non-treated and steam exploded barley, canola, oat and wheat straw using a pilot-scale pellet mill; and (Chapter 6)

7. to perform an overall energy analysis of the entire postharvest and densification process. (Chapter 7)

Chapter 9

9. Conclusions and Recommendations

9.1 Project Conclusions

All seven objectives set in Chapter 1 (section 1.7) were successfully achieved. An integrated approach to postharvest process (chopping, grinding and steam explosion), and feasibility study on lab-scale and pilot scale densification of non-treated and steam exploded barley, canola, oat and wheat straw was successfully established to develop baseline data and correlations, that assisted in performing overall specific energy analysis. A new procedure was developed to rapidly characterize the lignocellulosic composition of agricultural biomass using the Fourier Transform Infrared (FTIR) spectroscopy. In addition, baseline knowledge was created to determine the physical and frictional properties of non-treated and steam exploded agricultural biomass grinds. The significance of major contributing factors (independent variables such as biomass type, treatment, pressure and grind size) on pellet density, durability and specific energy was established. Also, an overall energy analysis of the entire postharvest and densification process was performed to determine whether a positive energy balance exists to justify using agricultural biomass as feedstock for production of biofuel.

Grinding experiments were conducted on non-treated and steam exploded barley, canola, oat and wheat straw using a forage chopper and a hammer mill (screen sizes of 30, 6.4, 3.2 and 1.6 mm) to determine specific energy requirements, and geometric mean particle size and distribution of ground material. It was determined that the bulk density of non-treated biomass was significantly higher than steam exploded agricultural biomass since application of steam explosion pre-treatment resulted in disintegration of organized lignocellulosic structure into finer components. For non-treated agricultural straw, the particle density of canola and oat straw significantly increased with a decrease in hammer mill screen size from 30 to 1.6 mm. The particle density of steam exploded barley and oat straw was significantly higher than non-treated straw. Specific energy required by hammer mill to grind non-treated and steam exploded barley,

canola, oat and wheat straw showed a negative power correlation with hammer mill screen sizes. From the test of normality and particle size distribution, it was concluded that the non-treated barley straw at 1.6 mm hammer mill screen size, canola straw, oat straw, and wheat straw at 3.2 mm hammer mill screen size resulted in grinds that would potentially produce better compacts. For steam exploded agricultural biomass, barley, canola and wheat straw at 6.4 mm hammer mill screen size, and oat straw at 1.6 mm screen size would potentially produce better compacts.

Rapid and cost effective quantification of lignocellulosic components (cellulose, hemicelluloses and lignin) of agricultural biomass (barley, canola, oat and wheat) is essential to determine the effect of various pre-treatments (such as steam explosion) on biomass used as feedstock for the biofuel industry. Fourier Transformed Infrared (FTIR) spectroscopy was considered as an option to achieve this objective. A novel procedure to quantitatively predict lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat straw was developed using FTIR spectroscopy, which can be easily extended for any form of lignocellulosic biomass. Regression equations having R^2 values of 0.89, 0.99 and 0.98 were developed to predict the cellulose, hemicelluloses and lignin compounds of biomass, respectively. The average absolute difference in predicted and measured cellulose, hemicellulose and lignin in agricultural biomass was 7.5%, 2.5%, and 3.8%, respectively.

During storage and handling, accurate knowledge of the physical and frictional behavior of biomass grinds is essential for the efficient design of equipment. Therefore, experiments were performed on non-treated and steam exploded barley, canola, oat and wheat straw grinds to determine their coefficient of internal friction and cohesion at three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm, three normal stress values of 9.8, 19.6 and 39.2 kPa at 10% moisture content (wb). At any specific hammer mill screen size, the geometric mean particle size and bulk density of non-treated straw was significantly larger than steam exploded straw. The bulk density of ground straw significantly increased with a decrease in hammer mill screen sizes. The steam exploded straw grinds resulted in higher coefficient of internal friction compared to non-treated straw grinds primarily because of lower bulk densities. Power, logarithmic or exponential equations were developed to predict the coefficient of internal friction and cohesion with respect to average geometric mean particle diameters for non-treated and steam explode barley, canola, oat and wheat straw grinds.

Compaction of low bulk density agricultural biomass is a critical and desirable operation for sustainable and economic availability of feedstock for biofuel industry. A comprehensive study of the compression characteristics (density of pellet and total specific energy required for compression) of ground non-treated and steam exploded barley, canola, oat and wheat straw obtained from three hammer mill screen sizes of 6.4, 3.2 and 1.6 mm at 10% moisture content (wb) was conducted. Four preset pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were applied using an Instron testing machine to compress samples in a cylindrical die. Ground steam exploded barley straw at screen sizes of either 3.2 or 1.6 mm produced high density compacts, while ground steam exploded canola, oat and wheat straw at screen sizes of 6.4, 3.2 or 1.6 mm produced high density compacts. Steam exploded barley straw for 3.2 mm at 138.9 MPa produced compacts having 13% higher density and consumed 19% lower total specific energy compared to non-treated straw. Steam exploded canola straw for 1.6 mm at 138.9 MPa produced compacts having 13% higher density and consumed 22% higher total specific energy compared to non-treated straw. Steam exploded oat straw for 3.2 mm at 94.7 MPa produced compacts having 19% higher density and consumed 13% higher total specific energy compared to non-treated straw. Steam exploded wheat straw for 6.4 mm at 138.9 MPa produced compacts having 17% higher density and consumed 17% higher total specific energy compared to non-treated straw. Three compression models, namely: Jones model, Cooper-Eaton model, and Kawakita-Ludde model were considered to determine the pressure-volume and pressure-density relationship of non-treated and steam exploded straws. Kawakita-Ludde model provided the best fit to the experimental data having R^2 values of 0.99 for non-treated straw and 1.00 for steam exploded biomass samples. The steam exploded straw had higher porosity than non-treated straw. In addition, the steam exploded straw was easier to compress since it had lower yield strength or failure stress values compared to non-treated straw.

For lab-scale pelleting, the statistical analysis indicated that type of agricultural biomass did not have any significant effect on pellet density, while steam explosion pretreatment, applied pressure and screen size had significant effect. However, pellet durability and specific energy required to densify agricultural straw were significantly affected by the type of agricultural biomass, steam explosion pretreatment, applied pressure and screen sizes. It has been concluded that the applied pressure (60.4%) was the most significant factor effecting pellet density followed by the application of steam explosion pre-treatment (39.4%). Similarly, the application of steam

explosion pre-treatment (55.7%) was the most significant factor effecting pellet durability followed by the grind size (38.9%). Also, the applied pressure (58.3%) was the most significant factor effecting specific energy required to manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar effect affect on specific energy. In addition, correlations for pellet density and specific energy with applied pressure and hammer mill screen sizes having highest R^2 values were developed. Higher grind sizes and lower applied pressures resulted in higher relaxations (lower pellet densities) during storage of pellets.

Pilot scale pelleting experiments were performed on non-treated and steam exploded barley, canola, oat and wheat straw grinds obtained from 6.4, 3.2, 1.6 and 0.8 mm hammer mill screen sizes at 10% moisture content (wb). During pilot scale pelleting, customization of ground straw material was performed by adding steam exploded biomass in increments of 25% to non-treated ground straw for respective biomass at specific grind size. Ground straw samples were conditioned to 17.5% moisture content and 10% flaxseed oil was added to increase the bulk density and flowability of grinds, which resulted in the production of pellets. The pilot scale pellet mill produced pellets from ground non-treated straw at hammer mill screen sizes of 0.8 and 1.6 mm and customized samples having 25% steam exploded straw at 0.8 mm. It was observed that the pellet bulk density and particle density are positively correlated. The density and durability of agricultural straw pellets significantly increased with a decrease in hammer mill screen size from 1.6 mm to 0.8 mm. Interestingly, customization of agricultural straw by adding 25% of steam exploded straw by weight resulted in higher durability (> 80%) pellets but did not improve durability compared to non-treated straw pellets. In addition, durability of pellets was negatively correlated to pellet mill throughput and was positively correlated to specific energy consumption.

An overall specific energy analysis was performed for post-harvest processing and pilot-scale densification of non-treated and customized (75% non-treated + 25% steam exploded) barley, canola, oat and wheat straw at 1.6 and 0.8 mm hammer mill screen sizes. On average, the operation of biomass chopper required five times more energy than chopping of biomass. Contrarily, the grinding of biomass required on an average three times more energy than operation of hammer mill. Interestingly, almost same amount of energy was required to operate

the pellet mill and production of pellets. Total specific energy required to form pellets increased with a decrease in hammer mill screen size from 1.6 to 0.8 mm and also the total specific energy significantly increased with customization of straw at 0.8 mm screen size. Pellet mill consumed the highest proportion of total specific energy followed by hammer mill, cooler and chopper for non-treated barley straw at 1.6 mm grind size. A decrease in grind size to 0.8 mm for non-treated straw significantly increases the proportion of hammer mill contribution. The most significant factor for customized straw is the specific energy required for steam explosion pre-treatment followed by pellet mill. It has been determined that the net specific energy available for production of biofuel is a significant portion of original agricultural biomass energy (89-94%) for all agricultural biomass. Almost, similar amount of specific energy is required to produce pellets from barley, canola, oat and wheat straw grinds. Customized pellets having steam exploded straw required more energy to manufacture resulting in availability of only 89% of total energy for biofuel production.

9.2 Project Recommendations

An integrated approach involving securing of baled straw from agricultural fields, size reduction (chopping and grinding), application of pre-treatment (steam explosion), determining the physical and frictional properties of straw grinds, lignocellulosic characterization of straw, densification of grinds into pellets to determine the effect of various independent parameters on quality (density and durability), and energy analysis / balance is critical to assess the technical and economic feasibility of the entire post-harvest and densification process.

The regression equations developed to predict frictional and mechanical properties of agricultural straw can be used to enhance process efficiency by eliminating the need for experimental procedure while designing and manufacturing of new handling equipment. Similarly, the regression equations developed to predict specific energy required for size reduction and properties of ground agricultural can be used by biorefineries to select appropriate equipment and perform economic feasibility of establishing a processing plant.

A novel process to rapidly predict the quantity cellulose, hemicellulose and lignin composition of agricultural biomass was developed using Fourier Transform Infrared Spectroscopy (FTIR). It is envisioned that the new procedure will bring unique perspective to the post-harvest processing of biomass and will enhance process efficiency and bring economic benefits to the manufacturer.

For lab-scale pelleting, the statistical analysis indicated that type of agricultural biomass did not have any significant effect on pellet density, while steam explosion pretreatment, applied pressure and screen size had significant effect. However, pellet durability and specific energy required to densify agricultural straw were significantly affected by the type of agricultural biomass, steam explosion pretreatment, applied pressure and screen sizes. It was also determined that the applied pressure (60.4%) was the most significant factor effecting pellet density followed by the application of steam explosion pre-treatment (39.4%). Similarly, the application of steam explosion pre-treatment (55.7%) was the most significant factor effecting pellet durability followed by the grind size (38.9%). Also, the applied pressure (58.3%) was the most significant factor effecting specific energy required to manufacture pellets followed by the biomass (15.3%), pre-treatment (13.3%) and grind size (13.2%), which had lower but similar effect affect on specific energy.

The quality (density and durability) of pellets obtained from lab-scale tests can also be correlated to the particle size distribution and test of normality performed in Chapter 2. The analysis concludes that irrespective of particle size distribution, the density of pellet is dictated by the applied pressure. However, at constant pressure, the density of pellets will be higher at lower grind sizes. Contrarily, the durability of pellet is significantly affected by the particle size distribution, which is higher at higher grind sizes. This is primarily due to interlocking of fibrous structure of material in addition to particle-particle binding.

Pilot-scale pelleting has posed different set of practical concerns, primarily associate with lower bulk density and poor flowability of ground straw through pellet mill, which continuously clogged without producing any pellets. These results do not completely agree with lab-based tests (compression and compaction analysis) in Chapter 5, where density and durability of steam exploded straw was significantly higher than non-treated straw. This warrants the need to design new pilot-scale pelleting technology and development of new procedure since existing technology seems to over-work on the low bulk density straw and results in clogging of pellet

mill. Alternatively, pre-compression of straw grinds needs to be investigated as an alternative to increase their bulk density and flowability through the pellet mill. In addition, steam conditioning of higher grind sizes should be explored that could result in production of pellets. However, an overall energy balance study is required to determine a trade-off between using steam conditioning or pre-compression vs. energy saved during hammer mill grinding of straw to large grind sizes.

Finally, it was observed that similar amount of specific energy is required during pilot-scale pelleting of barley, canola, oat and wheat straw grinds into high quality pellets. Therefore, biofuel pellet manufacturers should focus on increasing the pellet bulk density and durability since comparable amount of specific energy is required at any specific grind size and pretreatment. Pellet mill consumed the highest proportion of total specific energy followed by hammer mill, cooler and chopper for non-treated barley straw at 1.6 mm grind size. A decrease in grind size to 0.8 mm for non-treated straw significantly increases the proportion of hammer mill contribution. The most significant factor for customized straw is the specific energy required for steam explosion pre-treatment followed by pellet mill. Also, it is recommended to develop or use pellet mills that could pellet agricultural straw grinds obtained from higher hammer mill screen sizes (>1.6 mm) to increase the net available specific energy for production of biofuels.

Chapter 10

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Appendix A

A. Preliminary Findings of Fourier Transfrom Infrared Spectroscopy (FTIR) Experiments (Chapter 4)

A similar version of this Appendix has been presented and published at the CSBE/ CSBE/SCGAB the 17th World Congress of the International Commission of Agricultural Engineering (CIGR):

- Adapa, P.K., L.G. Tabil, G.J. Schoenau, T. Canam, M. Gruber and T. Dumonceaux. 2010. Application of infrared spectromicroscopy to characterize and determine lignocellulosic components in agricultural straw. CSBE/SCGAB the 17th World Congress of the International Commission of Agricultural Engineering (CIGR), Quebec City, Quebec, Paper No. CSBE100647, June 13-17: CSBE

A.1 Abstract

Rapid and cost effective quantification of lignocellulosic components (cellulose, hemicelluloses and lignin) of agricultural biomass (barley, canola, oat and wheat) is essential to determine the effect of various pre-treatments (such as steam explosion) on biomass used as feedstock for biofuel industry. Fourier Transformed Infrared (FTIR) spectroscopy was considered as an option to achieve this objective. Linear and exponential equations were developed to predict the lignocellulosic composition of biomass using mixtures of pure cellulose, hemicelluloses and lignin compounds. Equations having R^2 values of 0.83, 0.96 and 0.79 were obtained for

cellulose, hemicelluloses and lignin contents, respectively. Average multiplying factors of 0.4, 0.8 and 0.2 for cellulose, hemicelluloses and lignin, respectively were used to determine the predicted values since initial predicted values from equations were significantly higher than the measured composition of agricultural biomass. A close trend in variation in predicted values with respect to measured data for cellulose, hemicelluloses and lignin was observed having an absolute average difference of 3%.

A.2 Introduction

Agricultural (lignocellulosic) biomass residues such as barley, canola, oat and wheat straw have the potential to be used as the feedstock for the biofuel industry (Liu et al., 2005). After harvest, the low bulk density straw has to be processed and densified for efficient handling and transportation, and reap the potential economic benefits.

It has been reported by Sokhansanj et al. (2005) that densified straw often results in poorly formed pellets or compacts, and are difficult to handle and costly to manufacture. This is primarily due to the lack of complete understanding on the binding characteristics of biomass at the molecular level. The natural binding characteristics of lignocellulosic biomass can be enhanced by modifying the structure of cellulose-hemicellulose-lignin matrix by application of pre-processing and pre-treatment methods (Sokhansanj et al., 2005). However, the effect of various pre-processing and pre-treatment methods on the lignocellulosic matrix at the molecular level is not well understood. Applications of pre-processing methods such as size reduction or increasing porosity, and pre-treatment techniques such as steam explosion and pulse electric field on agricultural biomass have demonstrated an improvement in pellet (compact) quality that can be attributed to the changes in the lignocellulosic components and distribution (Ade-Omowaye et al., 2001; Bagby, 1982; Bhazal et al., 2003; Focher et al., 1998). Therefore, it is critical to quantitatively and rapidly determine the change in cellulose, hemicelluloses and lignin components of biomass due to application of pre-treatment methods.

Infrared spectroscopy has the potential to produce qualitative and quantitative analytical data for samples with minimum or no sample preparation, and at high speed and throughput (Budevska,

2002; Luypaert et al., 2003; Smola and Urleb, 2000; Tucker et al., 2000). Traditionally, chemical analyses of the individual components (e.g., lignin) of lignocellulosics have been performed by acid hydrolysis followed by gravimetric determination of lignin (Kelley et al., 2004). These methods can provide highly precise data. However, these methods are laborious, time-consuming, and, consequently, expensive to perform and sample throughput is limited. Hence, there is a need to develop analytical tools that can be used to rapidly and inexpensively measure the chemical composition of biomass (Gelbrich et al., 2009; Kelley et al., 2004; Vazquez et al., 2002).

One of the early studies on quantitative analysis of component mixtures of acetylsalicylic acid, salicylic acid and filler or binder with varying concentration using Fourier transform infrared (FTIR) photoacoustic spectroscopy (PAS) was performed by Rosenthal et al. (1988). They were able to develop partial least square models with high correlation coefficients. Another study by Belton et al. (1987) successfully used FTIR spectroscopy for the quantitative analysis of protein and starch mixtures. Similarly, Moh et al. (1999) used FTIR spectroscopy to investigate and develop a foundation for the rapid determination of β-carotene content of crude palm oil. They have also developed separate partial least squares calibration models to predict β-carotene based on spectral region from 976 to 926 cm^{-1} for FTIR spectroscopy. The use of infrared spectroscopy in the study of fats and oils has been reviewed by Guillen and Cabo (1997). Van de Voort et al. (1994) developed FTIR spectroscopy that operates in the mid infrared region (4000-400 cm^{-1}) and has been proven to be a powerful tool for quantitative analysis of fats and oils.

Rodrigues et al. (1998) have obtained linear correlation with high regression coefficients to estimate lignin content in Eucalyptus globulus wood, using bands characteristic for lignin in FTIR spectra and bands characteristic for carbohydrate as reference. Similarly, the estimate of lignin and polysaccharide content in eucalyptus and pine acetosolv pulps was performed by Vazquez et al. (2002) using FTIR spectroscopy to obtain mathematical models. They have employed a STEPWISE regression analysis for the selection of spectra bands that correlate satisfactorily with experimental results.

The characterization and stages of organic municipal solid waste matter decomposition during mechanical and biological treatment was determined using the FTIR spectroscopy (Smidt and Schwanninger, 2005). The technique was used to observe the maturity and stability of waste organic matter based on the missing spectral bands that indicate metabolic activities.

Tucker et al. (2000) successfully performed the analysis of glucose, mannose, xylose, and acetic acid using FTIR spectroscopy in conjunction with high-performance liquid chromatography quantitative analysis on liquors from dilute-acid-pretreated softwood and hardwood slurries. Similarly, Bjarnestad and Dahlman (2002) employed the FTIR PAS technique in combination with partial least square analysis to accurately predict the contents of carbohydrates in hardwood and softwood pulps. In addition, the analytical procedure developed could be used on a routine basis to quantify pulp constituents with considerably less effort and in shorter time than is possible using chemical analysis. Also, Nuopponen et al. (2005) successfully studied the chemical modification of Scots pine wood in thermal treatments in the range of 100-240^{o}C using the FTIR technique with the assistance of PAS detector. They have established that lignin became partly extractable by acetone at 180^{o}C and the amount of soluble lignin increased with an increase in temperature up to 220^{o}C. In addition, degradation of hemicelluloses was also detected from the FTIR spectral data.

Gelbrich et al. (2009) characterized the bacterial degradation of waterlogged softwood samples using FTIR spectroscopy. They have established a linear relationship between lignin content and the extent of bacterial degradation in softwood.

The literature review of lignocellulosic biomass have indicated that infrared spectroscopy could be used successfully to study the chemical structure of cellulose, hemicellulose and lignin in various agricultural biomasses as applied to food, feed, biocomposite, textile, and paper and pulp industries. It is evident from previous studies that FTIR spectroscopy has the potential to perform qualitative and quantitative analysis of agricultural (lignocellulosic) biomass using infrared spectroscopy that could be used to determine change in cellulose-hemicellulose-lignin composition prior to and after application of various pre-processing and pre-treatment methods. Therefore, the objective of this work was to estimate critical parameters in analytical specification of lignocellulosic biomass and consequently, to develop and validate a rapid

method for the qualitative and quantitative analysis of cellulose-hemicellulose-lignin composition of non-treated and steam exploded barley, canola, oat and wheat straw using FTIR PAS.

A.3 Materials and Method

A.3.1 Sample Material Preparation

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for FTIR spectroscopy experiments. The straw samples were acquired in square bale form during the summer of 2008 from the Central Butte area of Saskatchewan, Canada. The moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (w.b.), respectively. The moisture content was determined using ASABE Standard S358.2 (ASABE, 2008).

The non-treated straw samples were manually chopped using a pair of scissors and subsequently fine-ground in a precision grinder (Falling Number, Model No. 111739, Huddinge, Sweden) having a screen size of 1.0 mm. The steam explosion of straw was performed at the FPInnovations, Forintek pilot plant continuous steam explosion facility at Quebec City, Quebec. The Andritz (ANDRITZ AG, Graz, Austria) pressurized disc refiner having a plate gap of 0.5 mm, powered by a 160 kW (215 hp) motor with a variable speed drive set to operate at 2000 rpm was used to steam explode the straw. Similar to non-treated straw, the steam exploded straw was ground in a precision grinder having a screen size of 1.0 mm.

A.3.2 Reference Material Preparation

Quantitative analysis of cellulose, hemicelluloses and lignin composition of non-treated and steam exploded sample material is critical in order to predict and evaluate the change in natural binding characteristics of straw. Therefore, pure cellulose (microcrystalline powder), hemicelluloses (xylan from birch wood) and lignin (hydrolytic) powders were obtained from Sigma-Aldrich Canada Ltd. (St. Louis, MO, USA), and were subsequently mixed in different proportions (Table A.1) to determine the relationship (predictive models) between their

respective quantity in the mixture and representative FTIR spectra. Carbon black powder reference spectrum was used to correct for FTIR wavenumber-dependent instrumental effects.

Table A.1: Pure cellulose, hemicelluloses and lignin mixtures used to obtain reference spectra.

Reference Mixtures	Lignin (%)	Cellulose (%)	Hemicellulose (%)
C1H0L0*	100	0	0
C0H1L0	0	100	0
C0H0L1	0	0	100
C5H2L2	50	25	25
C2H5L2	25	50	25
C2H2L5	25	25	50
C7H2L0	75	25	0
C2H7L0	25	75	0
C2H0L7	25	0	75
C0H2L7	0	25	75
C3H3L3	33	33	33
C7H0L2	75	0	25
C0H7L2	0	75	25

*Note: C, H and L represents Cellulose, Hemicellulose and Lignin, respectively

A.3.3 Lignocellulosic Composition of Agricultural Biomass

It is essential to validate the predicted lignocellulosic quantity of sample agricultural straw (section 3.1) using correlation models developed from the analysis of reference material spectra (section 3.2). The experimental ligniocellulosic composition of agricultural straw was performed in replicates of three at the Agriculture and Agri-Food Canada, Saskatoon lab facility using the modified NREL LAP method for "Determination of Structural Carbohydrates and Lignin in Biomass" (Sluiter et al., 2008). This procedure uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. During this process, the lignin fractionates into acid insoluble material and acid soluble material, while the polymeric carbohydrates are hydrolyzed into the monomeric forms, which are soluble in the hydrolysis liquid and subsequently measured by HPLC (Waters Acquity UPLC, Waters, MA). Percentage cellulose in the samples was measured by using the percentage glucan content, while percentage hemicelluloses was measured by adding percentage mannose, galactose, xylose and arabinose

content in the biomass samples. Table A.2 provides information on the extractive removal and acid hydrolysis process adopted in the present experimental study.

Table A.2: Extractive removal and acid hydrolysis procedure for carbohydrate and lignin content determination in biomass.

Method	Experimental Steps
Extractive Removal	1. add sample to a filter paper pouch and seal 2. add pouch to a Soxhlet apparatus and reflux with acetone for 24 h 3. disassemble Soxhlet apparatus and oven-dry the samples in their pouches for 24 h
Acid Hydrolysis	1. add ~300 mg of oven-dried extractive-free sample to a 100 mL pressure tube (Ace Glass tube# 8648-88) 2. add 3 mL of 72% sulphuric acid and macerate/ mix with a glass rod every 10 min for 2 h 3. dilute acid to 4% by adding 84 mL of filtered water making sure to rinse off the glass rod completely to avoid material loss 4. screw on cap and autoclave for 1 h (2 h total run time) 5. cool tube to room temperature
Acid Hydrolysis – Insoluble Lignin Content	1. assemble a 250 mL side-arm flask vacuum filtration device and filter the hydrolysis suspension through a medium-coarseness 30 mL Pyrex crucible (pre-weighed after oven-dry) 2. disassemble the vacuum device and set aside an aliquot of the filtered hydrolysate (~20 mL) (see sections 3.2 and 3.3) 3. reassemble the vacuum device and rinse ALL remaining solids from the tube into the crucible using distilled water 4. disassemble the vacuum device and oven-dry the crucible with retentate for 24 h 5. record mass of crucible with retentate and determine insoluble lignin percentage: $\%insoluble\ lignin\ content = \left\{1 - \frac{(dried\ sample - dried\ retentate)}{dried\ sample}\right\} \times 100$

Acid Hydrolysis – Soluble Lignin Content	1. add 1 mL of hydrolysate to a quartz cuvette and measure the absorbance at 240 nm (may differ depending on feedstock) using 4% sulphuric acid as a blank 2. dilute sample with 4% sulphuric acid if necessary to obtain an absorbance value of 0.3-1.0 (record dilution factor) 3. determine soluble lignin content: $$\%soluble\ lignin\ content = \left\{\frac{A_{240} \times 87\ mL \times dilution\ factor}{\varepsilon \times dried\ sample\ mass \times spec\ pathlength}\right\} \times 100$$ *where ε is the feedstock-dependent absorptivity constant with units of L g^{-1} cm^{-1}* *[see section 11.3 of* NREL LAP 'Determination of Structural Carbohydrates and Lignin in Biomass' (Sluiter et al., 2008)] **Note:** a caveat to this method of soluble lignin determination is that protein content can cause an overestimation of soluble lignin content.
Acid Hydrolysis – Monosaccharide Quantification	1. slowly add 1 g of CaCO3 to ~20 mL of hydrolysate while mixing, and let settle for ~5 min 2. carefully pour off ~10 mL of the liquid fraction into a 15 mL centrifuge tube (some slurry will be transferred as well) 3. spin tube at 1500 rpm for 2 min to pellet slurry 4. filter (0.2 μm) an aliquot of supernatant into a UPLC vial and seal with cap 5. run method pre-determined to resolve cell-wall monosaccharides • Waters Acquity UPLC-MS system • ***Sample prep:*** 100 μL of neutralized hydrolysate with 900 μL of 75% acetonitrile/25% methanol; filtered through 0.2 μm filter into a 2 mL UPLC vial • ***LC conditions:*** Acquity UPLC BEH Amide Column (1.7μm pore size, 2.1 x 50 mm); 0.25 mL min^{-1} flowrate; mobile phase A: 95% acetonitrile/5% isopropanol; mobile phase B: 80% acetonitrile/0.1% NH_4OH; gradient from 100% A to 100% B over 10 min, then gradient of 100% B to 100% A over 4 min (14 min total)

- ***MS conditions:*** 2.8 kV; 25 V (cone); 50 L h^{-1} (cone); gas flow 600 L h^{-1}; desolvation temperature 350°C; source temperature 120°C; dwell 0.08 s; SIR of rhamnose (163.2); SIR of mannose, glucose, galactose (179.2); SIR of xylose and arabinose (149.1)

6. correlate monosaccharide peak area to concentration using pre-determined regression equations from dilution series of monosaccharide standards
7. determine monosaccharide content:

$$\%xylose\ content = \left\{\frac{xylose\ concentration\ \times 87\ mL}{dried\ sample\ mass}\right\} \times 100$$

Note: glucose content roughly approximates cellulose content; however some of the glucose results from starch hydrolysis (can assume to be minimal)

A.3.4 Fourier Transformed Infrared (FTIR) Equipment

Mid-IR beamline (01B1-1, energy range: 4000 to 400 cm^{-1}) at the Canadian Light Source Inc. (CLS, University of Saskatchewan, Saskatoon SK, Canada) was used to collect IR data of reference compounds and fine-ground sample agricultural straw in replicates of three. The beamline has a MTEC Model 300 photoacoustic cell (MTEC Photoacoustic Inc., Ames, IA) for FTIR photoacoustic spectroscopy (FTIR PAS) of bulk samples. The FTIR spectra of reference and straw samples were recorded using Globar source (silicon carbide rod). The FTIR PAS determines the absorption of radiation by samples via measuring the changes in thermal expansion of gas surrounding the sample using a microphone (McClelland et al., 2002). The reference and straw samples were filled in the sample cup and purged with dry helium to remove water vapor and CO_2 from the sample chamber. The spectrum for each sample was recorded separately by averaging 32 interferograms collected from wavenumbers of 2000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

The OPUS 6.5 (Bruker Optics Inc., Billerica, MA) software was used to record and analyze the FTIR PAS data. The software Origin (version 7.5, OriginLab, Northampton, MA) was used to plot the data.

A.3.5 Quantitative Analysis Using FTIR Spectra

The quantitative analysis of absorption spectrometry is based on the Bouguer-Beer-Lambert law (Sherman Hsu, 1997). According to this law, for a single compound in a homogenous medium, the absorbance at any frequency is expressed as:

$A = abc$

where A is the measured sample absorbance at the given frequency, a is the molecular absorptivity at the frequency, b is the path length of source beam in the sample, and c is the concentration of the sample. The law implies that the intensities of absorption bands are linearly proportional to the concentration of each component in a homogenous mixture or solution (Sherman Hsu, 1997).

Therefore, a number of quantification parameters, which include peak height, peak area, and derivatives, were used in quantitative analysis. In this study, the authors have used peak height as the quantification parameter since preliminary analysis using peak area did not produce an identifiable trend and agreeable results.

A.3.5.1 Peak Height Method

Three types of spectral plots were developed. The first plot has spectral information of pure (100%) cellulose, hemicelluloses and lignin in order to identify characteristic peaks of respective components. One of the distinguishable characteristic peaks of individual components was chosen to measure the peak height. The height of the peak (intensity of maximum absorption) was measured by calculating the difference between the peak intensity of the absorption band and value of intensity at the foot of the curve (Figure A.1). The corresponding wavenumber at peak intensity ($\overline{\nu}_{max}$) and foot of the absorption band ($\overline{\nu}_{min}$) was recorded.

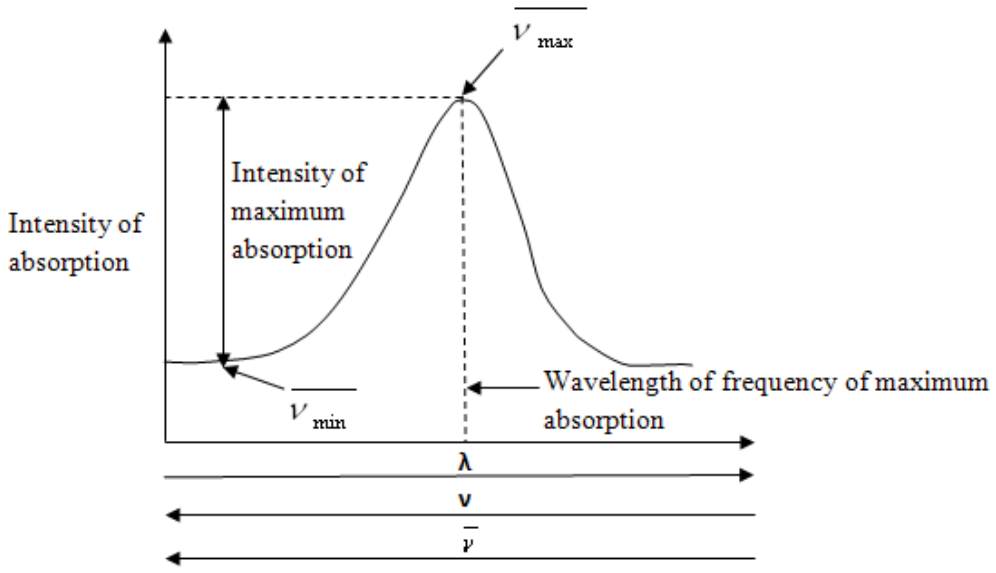


Figure A.1: Schematic of absorption spectra (Yadav, 2005) (Note: λ is wavelength, ν is frequency and $\overline{\nu}$ is wavenumber of IR radiation).

The second plot has spectral information of reference compound mixtures as indicated in Table A.1. The wavenumbers recorded for cellulose, hemicelluloses and lignin from the first spectral plot was used as the guide to calculate the characteristic peak height for respective component in the reference compound mixtures. Thereafter, the trend in variation of peak height of cellulose, hemicellulose and lignin components in the mixture was correlated to their percentage composition. Subsequently, predictive models for cellulose, hemicelluloses and lignin were developed that has the capability to predict quantity (percentage composition) of cellulose, hemicelluloses and lignin in agricultural biomass.

The third plot provided spectral information of sample biomass materials, which were used to extract qualitative information of various chemical components. In addition, wavenumbers recorded from the first plot were used to measure the characteristic peak height for cellulose, hemicelluloses and lignin component in the fine-ground non-treated and steam exploded straw sample spectra. The peak height values obtained from plot three were inserted in the developed models to predict percentage composition of lignocellulosic components in the non-treated and steam exploded barley, canola, oat and wheat straw.

A.3.5.2 Data Normalization Procedure

The agricultural biomass samples FTIR spectra intensity data were corrected for any wavenumber-dependent instrumental effects through division by carbon black reference spectrum intensity. This strategy implicitly assumes that the stability of the instrumentation used is adequate to ensure reliable results, even though the sample and reference spectra are acquired at different times (Michaelian, 2005). Also, the effect of reference and sample straw bulk density was eliminated by multiplying the data with ratio of maximum mass observed for any sample to respectively mass of sample contained in the PAS sample cup.

In order to further standardize the methodology, the carbon black and mass normalized FTIR data were normalized to 0 to 1 (intensity) by dividing the intensity spectra of individual biomass samples by corresponding maximum intensity value. Hence the normalization process ensures that the model is adaptable for quantitative analysis of FTIR spectra obtained for any lignocellulosic biomass.

A.4 Results and Discussion

A.4.1 Lignocellulosic Composition of Agricultural Biomass

Table A.3 shows the lignocellulosic composition of non-treated and steam exploded barley, canola, oat and wheat straw samples. In general, the cellulose, hemicelluloses and lignin content of steam exploded straw was higher than non-treated straw. This may be due to other components (soluble lignin, loosely-bound sugars) being washed away during steam explosion, thereby leaving the proportion of insoluble lignin, cellulose and hemicellulose in the resulting dried sample higher than for the non-treated samples (i.e. higher % of dry mass).

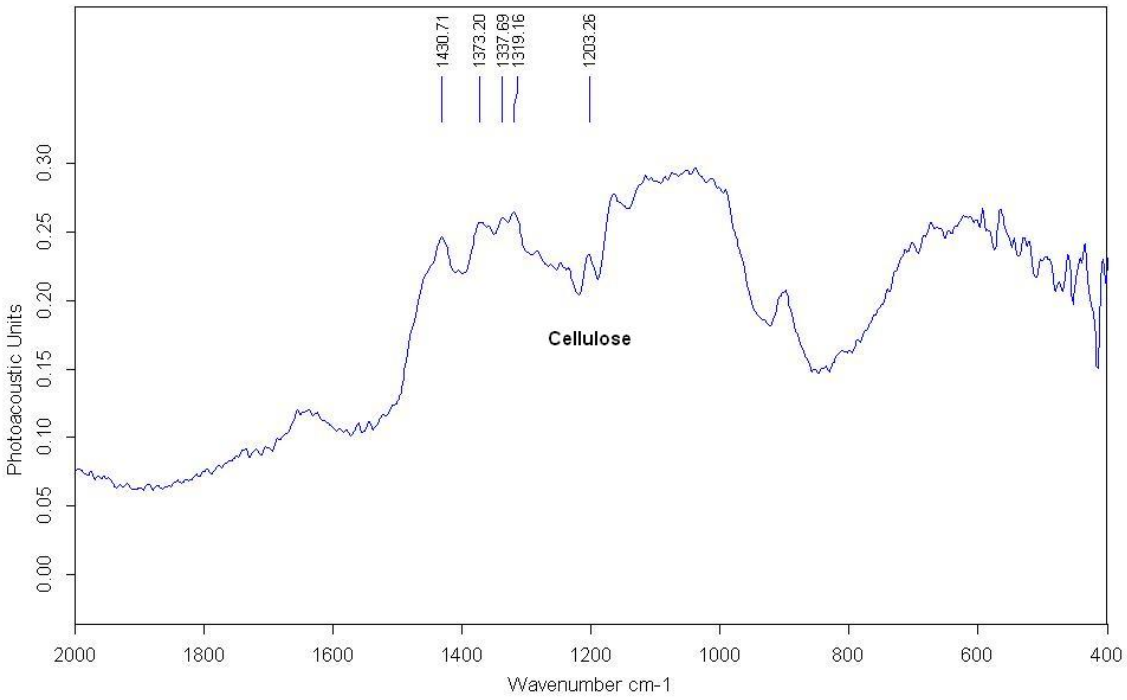
Table A.3: Lignocellulosic composition of non-treated and steam exploded agricultural straw

Composition (% DM)	Barley Straw		Canola Straw		Oat Straw		Wheat Straw	
	NT	SE	NT	SE	NT	SE	NT	SE
Cellulose[b]	**22.7 ± 0.9[a]**	**25.3 ± 1.8**	**22.4 ± 0.8**	**27.5 ± 1.1**	**25.4 ± 1.0**	**27.4 ± 2.4**	**27.1 ± 1.0**	**29.9 ± 1.4**
Hemicellulose[c]	**21.2 ± 0.5**	**21.0 ± 1.4**	**16.9 ± 0.5**	**20.2 ± 0.7**	**21.7 ± 0.9**	**18.8 ± 1.2**	**21.1 ± 0.5**	**19.7 ± 0.9**
a. Galactose	0.9 ± 0.0	0.7 ± 0.0	1.0 ± 0.0	0.9 ± 0.1	0.8 ± 0.0	0.7 ± 0.0	0.8 ± 0.0	0.9 ± 0.1
b. Mannose	1.6 ± 0.2	1.5 ± 0.0	2.3 ± 0.1	1.9 ± 0.4	1.4 ± 0.0	1.7 ± 0.1	1.6 ± 0.1	2.8 ± 0.2
c. Xylose	14.4 ± 0.3	15.3 ± 1.0	11.5 ± 0.5	14.3 ± 0.2	15.1 ± 0.8	13.3 ± 1.0	14.9 ± 0.4	13.5 ± 0.4
d. Arabinose	4.4 ± 0.2	3.5 ± 0.5	2.0 ± 0.1	3.2 ± 0.0	4.4 ± 0.2	3.1 ± 0.2	3.9 ± 0.1	2.6 ± 0.2
Total Lignin[d]	**21.0 ± 0.6**	**21.6 ± 0.6**	**19.6 ± 0.6**	**22.3 ± 0.2**	**19.5 ± 0.6**	**23.7 ± 0.2**	**22.5 ± 0.7**	**24.2 ± 0.3**
a. Soluble Lignin	1.6 ± 0.1	1.4 ± 0.1	1.6 ± 0.1	1.2 ± 0.1	1.5 ± 0.1	1.3 ± 0.1	1.4 ± 0.0	1.0 ± 0.1
b. Insoluble Lignin	19.4 ± 0.6	20.2 ± 0.6	18.0 ± 0.6	21.1 ± 0.1	17.9 ± 0.7	22.4 ± 0.1	21.0 ± 0.7	23.3 ± 0.4

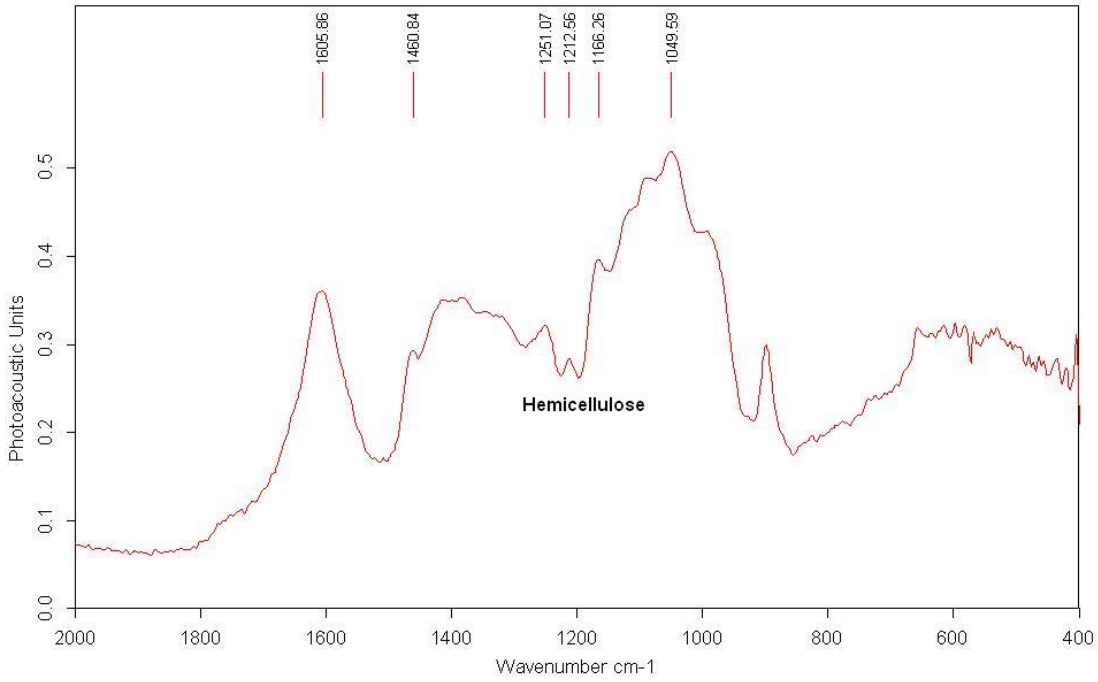
DM – Dry Matter; NT – Non-Treated; SE – Steam Exploded;
[a] Average and standard deviation of 3 replicates at 95% confidence interval;
[b]%Cellulose = %glucan;
[c]%Hemicellulose = %(mannose + galactose + xylose + arabinose);
[d]%Total Lignin = %(soluble lignin + insoluble lignin).

A.4.2 Reference Material Spectra

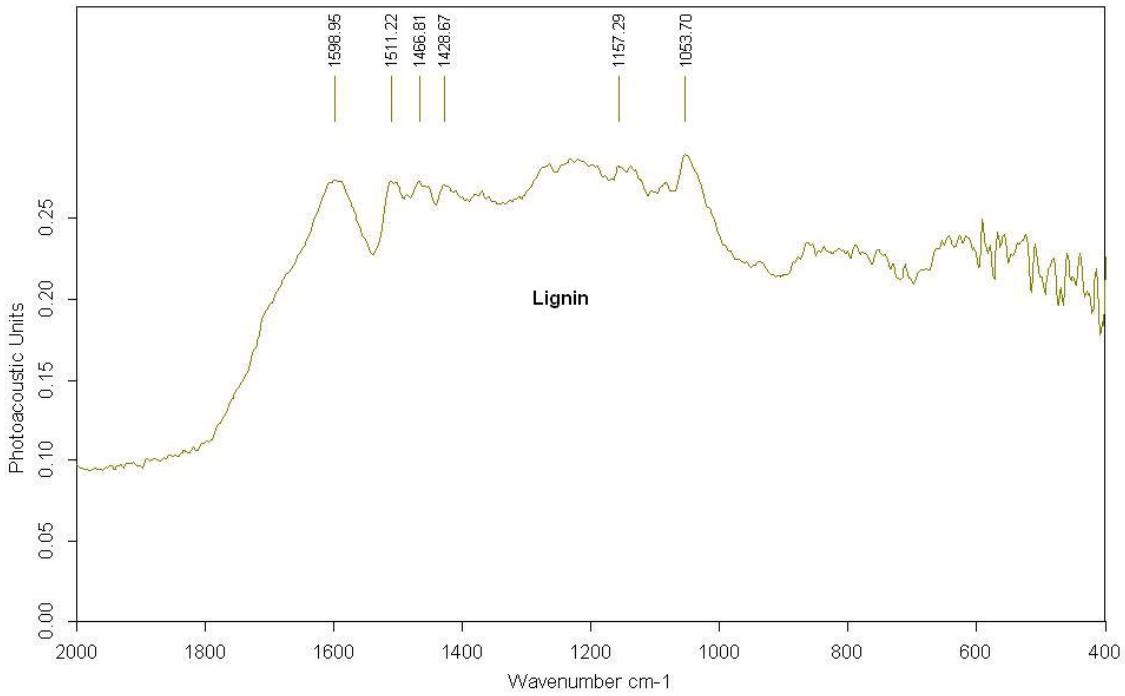
Figure A.2 represents the FTIR PAS spectra of pure cellulose, hemicellulose and lignin powder in the range of 2000 to 400 cm^{-1}. The characteristic/ prominent peaks for cellulose, hemicellulose and lignin, and their peak assignments are provided in Table 4. The cellulose spectrum has five distinct peaks at wavenumbers of 1431, 1373, 1338, 1319 and 1203 cm^{-1}. Similarly, hemicellulose (xylan) had prominent peaks at wavenumbers of 1606, 1461, 1251, 1213, 1166 and 1050 cm^{-1}. The lignin spectrum showed characteristic peaks at wavenumber of 1599, 1511, 1467, 1429, 1157 and 1054 cm^{-1}.



(A.2a) Cellulose 100%



(A.2b) Hemicellulose 100%



(A.2c) Lignin 100%

Figure A.2: FTIR PAS spectra of pure cellulose (microcrystalline powder), hemicelluloses (xylan from birch wood) and lignin (hydrolytic) powders

Table A.4: Characteristic/ prominent peaks of pure cellulose, hemicellulose and lignin, and their peak assignments

Wavenumbers (cm^{-1})	Cellulose 100%	Hemicellulose 100%	Lignin 100%	Peak Assignment
1650-1600	--	1606	--	1600 – quadrant ring stretching (aromatic lignin) (Colthup et al. 1990; Yu et al. 2007); 1600-1610 – aromatic skeletal vibration (Pandey 1999; Yu et al. 2007); 1635 – carbonyl stretching conjugate with aromatic rings (Cyran 2007)
1600-1550	--	--	1599	1595 – very strong aromatic ring stretch, aromatic C-O stretch (Revol 1982; Stewart et al. 1995); 1595 – phenylpropanoid polymer (Himmelsbach et al. 1998); 1595 – aromatic skeletal vibrations plus C=O stretch (Lin and

				Dence 1992)
1550-1500	--	--	1511	1510 – semicircle ring stretching (aromatic lignin) (Colthup et al. 1990; Yu et al. 2007; Yu 2005), 1510 – phenylpropanoid polymer (Himmelsbach et al. 1998); 1510 – very strong aromatic ring stretch, aromatic C-O stretch (Revol 1982; Stewart et al. 1995); 1513 – aromatic C=C stretch (Sun et al. 2005); 1514 – semi-circle stretch of para-substitute benzene rings (Lin-Vein et al. 1991; Budevska 2002); 1550 – protein (Budevska 2002)
1500-1450	--	1461	1467	1462 – C-H deformation (methyl and methylene) (Pandey 1999)
1450-1400	1431	--	1429	1420 – weak C-O stretching (Yu et al. 2007; Wetzel et al. 1998); 1430 – CH_2 in-plane bending vibrations (Schulz and Baranska 2007; Wilson et al. 2000); 1433 – aromatic C=C stretch (Sun et al. 2005)
1400-1350	1373	--	--	1370 – weak C-O stretching (Yu et al. 2007; Wetzel et al. 1998); 1380 – C-H symmetric and asymmetric deformation (Sun et al. 2005); 1382 – C-O stretch (Xu et al. 2007)
1350-1300	1319, 1338	--	--	1335 – weak C-O stretching (Yu et al. 2007; Wetzel et al. 1998); 1336 – C-H ring in-plane bending vibrations (Schulz and Baranska 2007; Wilson et al. 2000)
1300-1250	--	1251	--	1250 – Acetylated Hemicellulose (Himmelsbach et al. 1998)
1250-1200	1203	1213	--	1246 – weak C-O stretching (Yu et al. 2007; Wetzel et al. 1998); 1246 – Hemicellulose (Budevska 2002; Yu et al. 2007); 1250 – Acetylated Hemicellulose (Himmelsbach et al. 1998); 1250 – acetylated hemicelluloses (Budevska 2002)
1200-1150	--	1166	1157	1160 – glycosidic linkage (Robert 2005); 1162 – C-O-C ring vibrational stretching (Schulz and Baranska 2007; Wilson et al. 2000)

1100-1050	--	--	1054	1078 – β(1-3) polysaccharide (Szeghalmi et al. 2007); 1098 – weak absorbance (Stewart et al. 1995)
1050-1000	--	1050	--	1035 – C-O, C=C and C-C-O vibrational stretching (Schulz and Baranska 2007; Wilson et al. 2000); 1045 – C-OH bending (Wetzel et al 2003; Cyran 2007; Robert 2005); 1018 – galactomannans (Szeghalmi et al. 2007); 1025 – non-structural CHO (Yu et al. 2007)

A.4.3 Quantitative Analysis

After a careful analysis of the results, the authors decided to choose the characteristic peaks at wavenumbers of 1203, 1050 and 1512 cm^{-1} for cellulose, hemicellulose and lignin, respectively (Figure A.2). The heights of individual characteristic peaks were determined using the procedure described in materials and methods (section A.3.5.1). Table A.5 shows the wavenumbers at peak intensity ($\overline{\nu}_{max}$) and foot of the absorption band ($\overline{\nu}_{min}$) (Figure A.1).

Table A.5: Wavenumbers used to determine the height of characteristic peaks for cellulose, hemicellulose and lignin.

Component	Wavenumber (cm^{-1})	
	$\overline{\nu}_{min}$	$\overline{\nu}_{max}$
Cellulose	1192	1203
Hemicellulose	1148	1050
Lignin	1536	1512

Note: $\overline{\nu}_{max}$ = wavenumber at peak intensity of absorption band;

$\overline{\nu}_{min}$ = wavenumber at foot of the absorption band.

Subsequent to following the data normalization process described in section 3.5.2, the characteristic wavenumbers of cellulose, hemicelluloses and lignin from Table 5 were used to determine the peak height photoacoustic intensity for individual components in the reference mixtures (Table A.1). The percentage composition of cellulose, hemicelluloses and lignin were plotted in graphs (Figures A.3, A.4 and A.5) and correlation models (equations) were obtained by fitting appropriate curves with highest R^2 values.

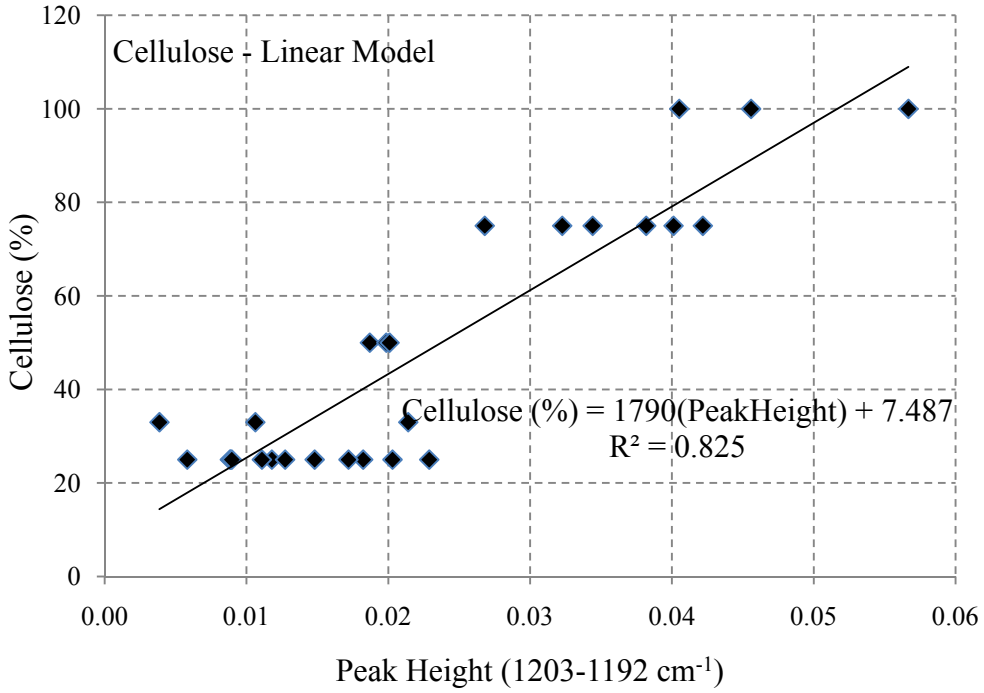


Figure A.3: Correlation between peak height and quantity of cellulose in the reference mixtures.

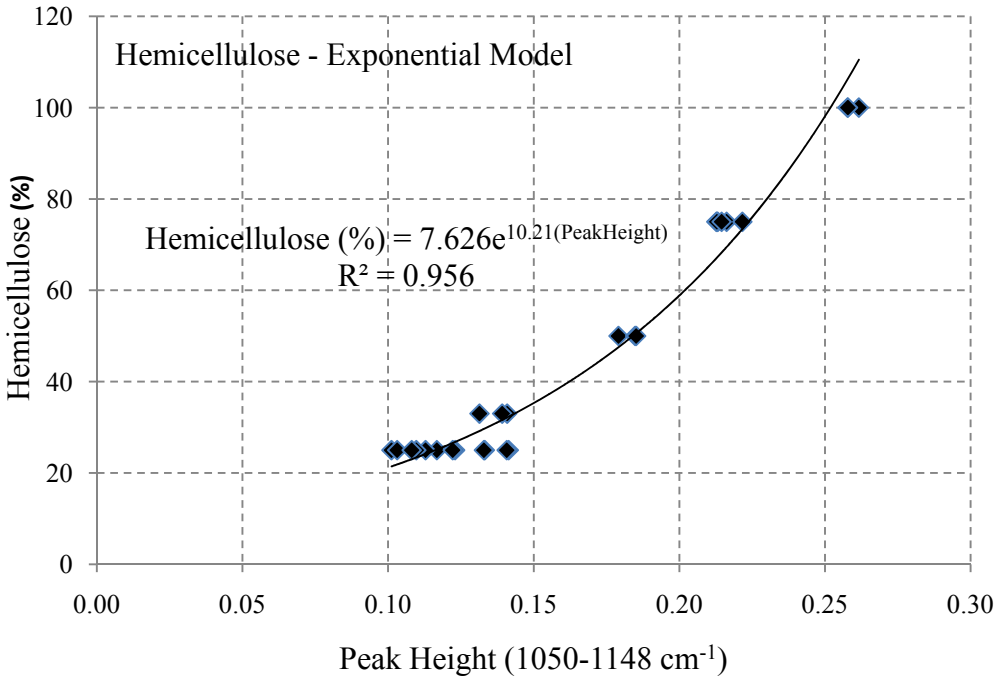


Figure A.4: Correlation between peak height and quantity of hemicellulose in the reference mixtures.

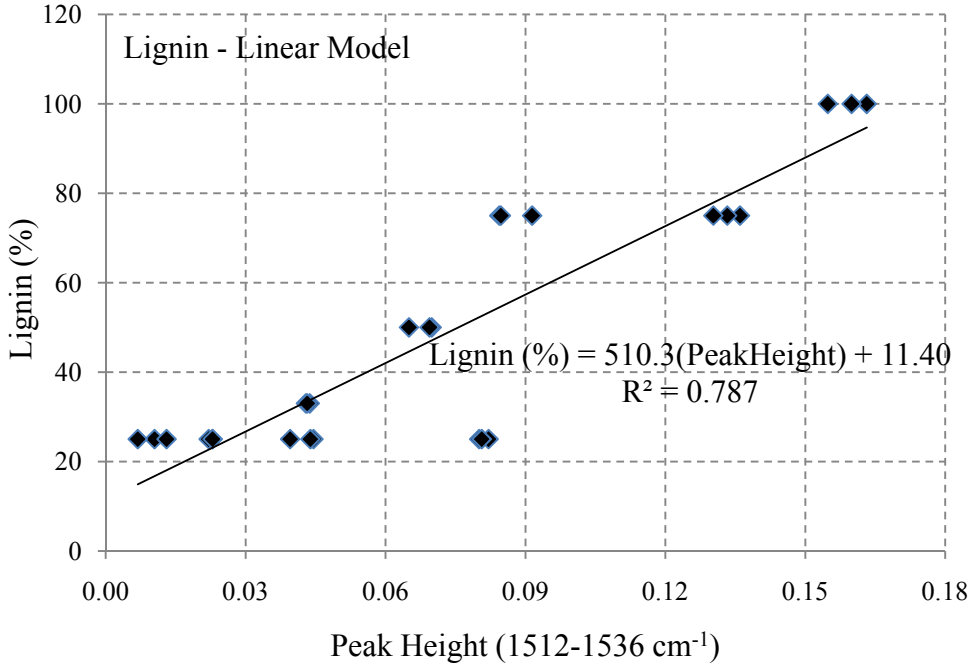


Figure A.5: Correlation between peak height and quantity of lignin in the reference mixtures.

A.4.4 Sample Material Spectra

The characteristic peak heights of cellulose, hemicellulose and lignin for barley, canola, oat and wheat straw samples were determined by using the wavenumbers provided in Table A.5 and following the procedure described in the materials and methods (section A.3.5.1). The peak height values were subsequently used to predict the percentage of lignocellulosic composition in the corresponding agricultural straw samples using the predictive models derived from Figures A.3, A.4 and A.5. It was observed that the predicted values were significantly higher than the measured composition of cellulose, hemicelluloses and lignin in the straw material. Therefore, average multiplying factors of 0.4, 0.8 and 0.2 for cellulose, hemicelluloses and lignin, respectively, were used to determine the final predicted values. The predicted and measured values of lignocellulosic components of barley, canola, oat and wheat straw (Table A.3) are plotted in Figures A.6, A.7 and A.8. All figures show a close trend in variation in predicted values with respect to measured data having the predicted values numerically different from measured values. The absolute average difference in measured and predicted values for cellulose, hemicelluloses and lignin was 3% (excluding value for non-treated canola for cellulose determination). This could be attributed to larger grind size of sample material as compared to reference material (Agarwal and Kawai, 2003). Sherman Hsu (1997) indicated that the deviation from the Bouguer-Beer-Lambert law often occurs in infrared spectroscopy. These deviations stem from both instrumental and sample effects. Assuming negligible instrumental effect, the sample effect will include chemical reactions and molecular interactions such as hydrogen bonding (Sherman Hsu, 1997).

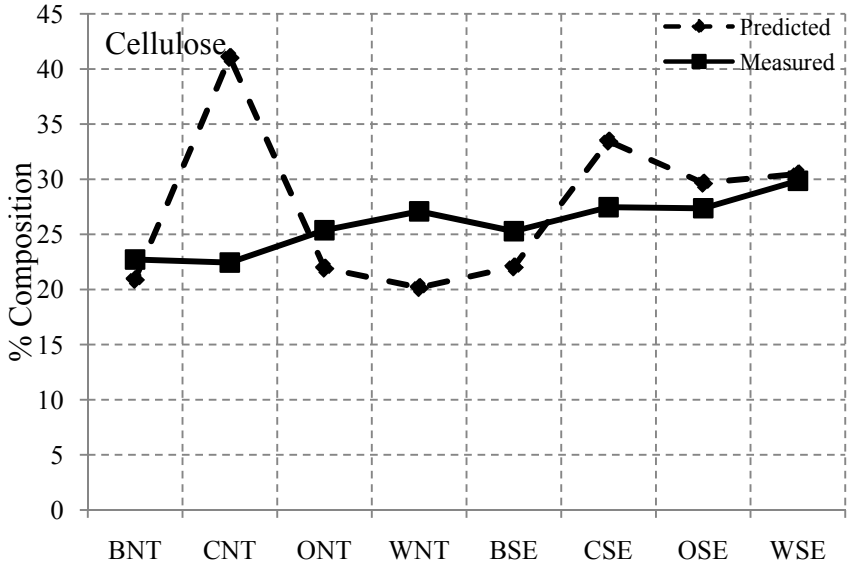


Figure A.6: Trend in variation of predicted values for cellulose with respect to measured data for non-treated (NT) and steam exploded (SE) Barley (B), Canola (C), Oat (O), and Wheat (W) straw samples.

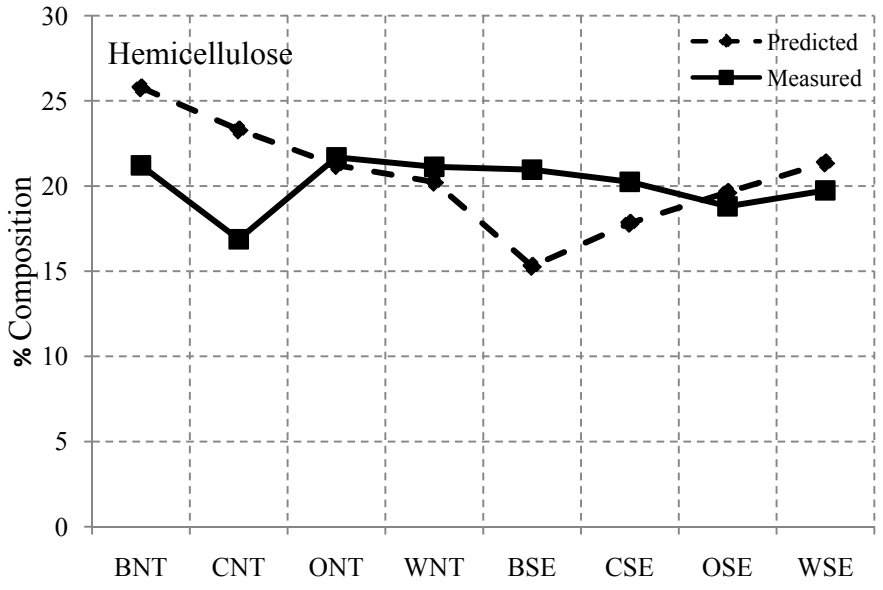


Figure A.7: Trend in variation of predicted values for hemicellulose with respect to measured data for non-treated (NT) and steam exploded (SE) Barley (B), Canola (C), Oat (O), and Wheat (W) straw samples.

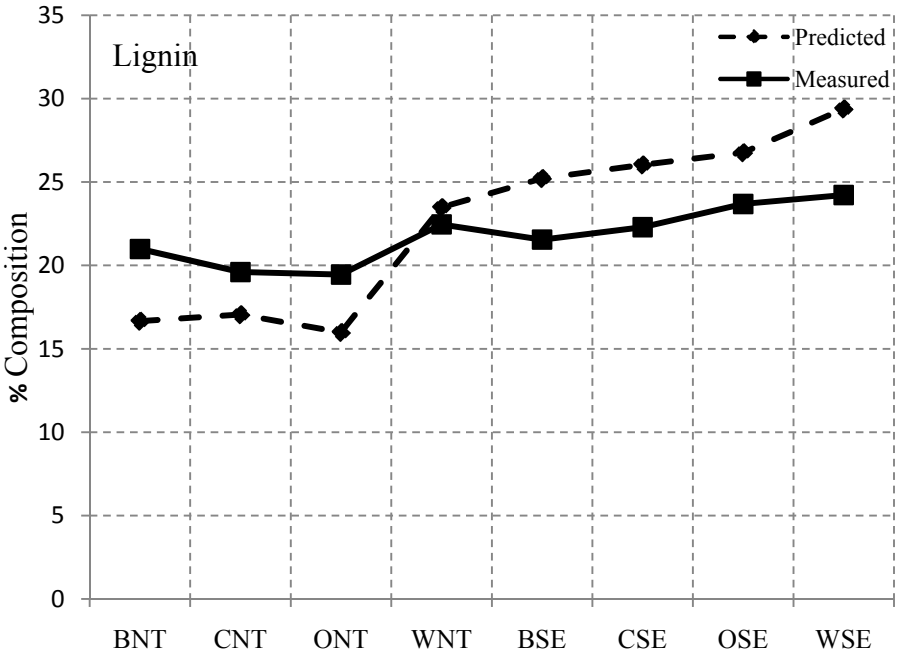


Figure A.8: Trend in variation of predicted values for lignin with respect to measured data for non-treated (NT) and steam exploded (SE) Barley (B), Canola (C), Oat (O), and Wheat (W) straw samples.

A.5 Conclusion

The authors successfully developed a procedure to quantitatively predict lignocellulosic components of non-treated and steam exploded barley, canola, oat and wheat straw, which could be easily extended for any form of lignocellulosic biomass using FTIR spectroscopy. The FTIR quantitative analysis of pure cellulose, hemicelluloses and lignin resulted in predictive equations having R^2 values of 0.83, 0.96 and 0.79, respectively. Average multiplying factors of 0.4, 0.8 and 0.2 for cellulose, hemicelluloses and lignin, respectively, were used to determine the final predicted values since initial predicted values from equations were significantly higher than the measured composition of agricultural biomass. The proposed equations are suitable to perform relative lignocellulosic composition analysis of biomass before and after application of pre-treatment. However, it is anticipated that there could be an absolute difference of 3% between measured and predicted values.

Appendix B

B. Comprehensive Review of Various Compression Models (Chapter 5)

A similar version of this Appendix has been published with the CIGR Ejournal:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2009. Compression characteristics of selected ground agricultural biomass. *Agricultural Engineering International: the CIGR Ejournal*, Manuscript 1347, XI(June): 1-19.

B.1 Abstract

Agricultural biomass such as barley, canola, oat and wheat straw has the potential to be used as feedstock for bioenergy. However, the low bulk density straw must be processed and densified in order to facilitate handling, storage and transportation. It is important to understand the fundamental mechanism of the biomass compression process, which is required in the design of energy efficient compaction equipment to mitigate the cost of pre-processing and transportation of the product. Therefore, a comprehensive review of various compression models was performed and the compression behavior of selected ground agricultural biomass was studied. Five compression models were considered to determine the pressure-volume and pressure-density relationship to analyze the compression characteristics of biomass samples, namely: Jones (1960), Heckle (1961), Cooper-Eaton (1962), Kawakita-Ludde (1971), and Panelli-Filho (2001), models. Densification studies were conducted on four selected biomass samples at 10% moisture content (wb) and 1.98 mm grind size using four pressure levels of 31.6, 63.2, 94.7 and 138.9 MPa. The mean densities of barley, canola, oat and wheat straw increased from 907 to

977 kg/m^3, 823 to 1003 kg/m^3, 849 to 1011 kg/m^3 and 813 to 924 kg/m^3, respectively. The Kawakita-Ludde model provided an excellent fit having R^2 values of 0.99 for selected agricultural straw samples. It was also concluded that the ground oat and canola straw had the highest level of porosity and failure stress, respectively. The parameters of Cooper-Eaton model indicated that the ground straw samples were densified easily by the particles rearrangement method and Jones model indicated that canola and oat straw were more compressible as compared to barley and wheat straw.

B.2 Introduction

Agricultural biomass such as barley, canola, oat and wheat straw has the potential to be used as feedstock for biofuel industry (Campbell et al., 2002; Sokhansanj et al., 2006). However, due to low bulk density of straw, agricultural biomass has to be ground and compacted into dense and durable pellets in order to facilitate handling, storage and transportation (Adapa et al., 2007; Mani et al., 2003). In addition, because of uniform shape and sizes, densified products can be easily adopted in direct-combustion or co-firing with coal, gasification, pyrolysis, and in other biomass-based conversions (Kaliyan and Morey, 2006a).

The compression characteristics of ground agricultural biomass vary under various applied pressures. It is important to understand the fundamental mechanism of the biomass compression process, which is required in the design of energy efficient compaction equipment to mitigate the cost of production and enhance the quality of the product (Mani et al., 2004). To a great extent, the strength of manufactured pellets depends on the physical forces that bond the particles together (Tabil and Sokhansanj, 1996). These physical forces come in three different forms during pelleting operations: a) thermal; b) mechanical; and c) atomic forces (Adapa et al., 2002).

Pellets are formed by subjecting the biomass grinds to high pressures, wherein the particles are forced to agglomerate. It is generally accepted that the compression process is categorized in several distinct stages and difficult to let one simple monovariate equation to cover the entire densification region (Sonnergaard, 2001). Compression of grinds is usually achieved in three stages (Holman, 1991). In the first stage, particles rearrange themselves under low pressure to form close packing. The particles retain most of their original properties, although energy is

dissipated due to inter-particle and particle-to-wall friction. During the second stage, elastic and plastic deformation of particles occurs, allowing them to flow into smaller void spaces, thus increasing inter-particle surface contact area and as a result, bonding forces like van der Waal forces become effective (Rumpf, 1962; Sastry and Fuerstenau, 1973; Pietsch, 1997). Brittle particles may fracture under stress, leading to mechanical interlocking (Gray 1968). Finally, under high pressure the second stage of compression continues until the particle density of grinds has been reached. During this phase, the particles may reach their melting point and form very strong solid bridges upon cooling (Ghebre-Sellassie, 1989). Figure B.1 shows the deformation mechanisms of powder particles under compression (Comoglu, 2007; Denny, 2002).

Johansson et al. (1995) and Johansson and Alderborn (1996) studied the compression behavior of pelletized microcrystalline cellulose and described the compression mechanism as primarily composed of permanent deformation (change in the shape of the individual particles) and densification (contraction of porosity reduction of the individual compacts), followed by minute fragmentation of the compacts (Alderborn and Wikberg, 1996).

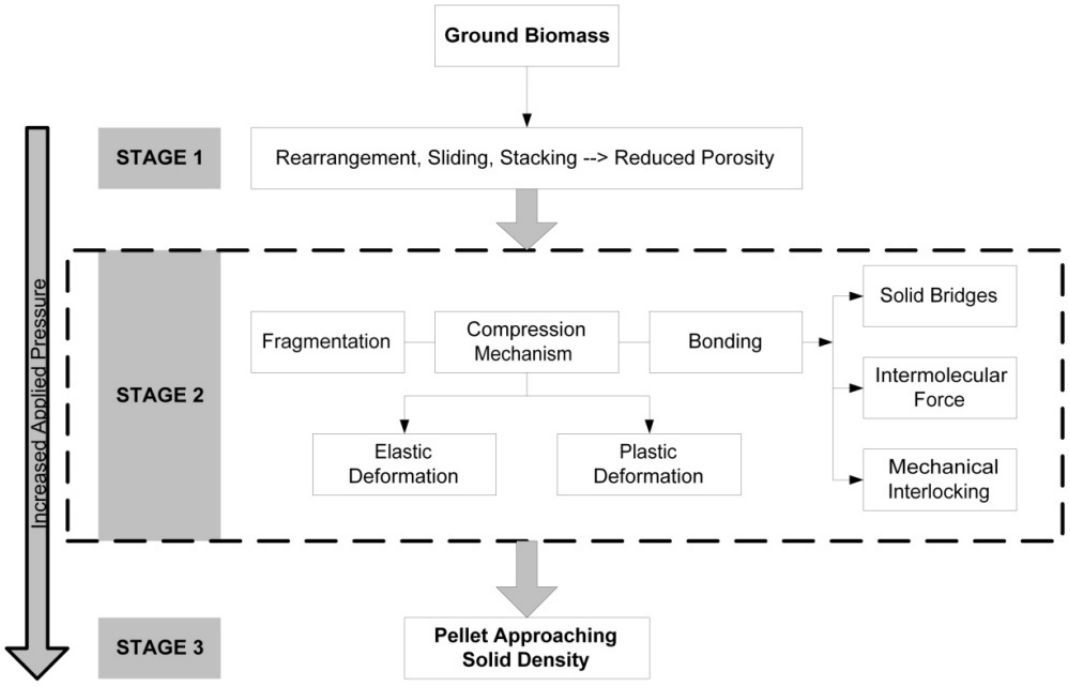


Figure B.1: The deformation mechanisms of powder particles under compression (Comoglu, 2007; Denny, 2002)

Biomass contains chemical compounds such as cellulose, hemicelluloses, protein, starch, lignin, crude fibre, fat, and ash. Protein plasticizes under heat and acts as a binder, which assists in increasing the strength of pelletized product (Winowiski, 1988; Briggs et al., 1999). In the presence of heat and moisture, gelatinization of starch occurs, which results in binding of ground biomass (Wood, 1987; Thomas et al., 1998). In addition, mechanical shearing during the densification process also improves starch gelatinization (Kaliyan and Morey, 2006a). At high temperatures and pressures, lignin softens and helps the binding process. Lignin has thermosetting properties and a low melting point of about 140^{o}C (van Dam et al., 2004). A similar compression mechanism involving chemical compounds was identified in the alfalfa pelleting process by Tabil and Sokhansanj (1996), for wheat straw, barley straw, corn stover and switch grass pelleting by Mani et al. (2004), and for fractionated alfalfa grinds by Adapa et al. (2002). Bilanski and Graham (1984) and O'Dogherty and Wheeler (1984) reported that at high compression pressures, biomass particles would be flattened/crushed damaging the cell structure and consequently releasing protein and pectin. These compounds would act as natural binders and aid the adhesion of biomass particles. Presence of natural binding compounds in the biomass particles is a major difference between biomass particles and ceramic or metallic or pharmaceutical powders (Kaliyan and Morey, 2006a).

Other differences of biomass particles include porosity, presence of multi-components (e.g. stem and leaf) with complex mechanical properties, and compressibility. Mohsenin (1986) reported that the major part of the residual deformation in biomass is due to the presence of pores or air spaces, weak ruptured cells on the surface, microscopic cracks, and other discontinuities which may exist in the structure of the material. This can be viewed as an analog to the phenomenon of slip and dislocation in metals due to imperfections in their crystal structures. These defects in crystal structures are believed to be responsible for plastic or permanent deformation which results from slip, or glide, of part of the body over the other (Kaliyan and Morey, 2006a).

Therefore, the objectives of the current study are to: 1) review various compression models; and 2) study compression behavior of ground agricultural biomass (barley, canola, oat and wheat straw) subjected to various pressures.

B.3 Review of Compression Models

Densification or compaction of various powders or grinds is an essential process to manufacture products including ceramics, metallic parts, fertilizers, pharmaceuticals and agricultural biomass (Comoglu, 2007; Mani et al., 2004; Panelli and Filho, 2001; Tabil, 1996). Ground particles (metallic or non-metallic) behave in different manner under different pressures. Therefore, it is important to study the change in compact density and volume under different pressures. One of the main purposes of fitting experimental data to an equation is usually to linearize the plots in order to make comparisons easier between different sets of data (Comoglu, 2007).

B.3.1 Walker Model

Walker (1923) reported a series of experiments on the compressibility of powders. He expressed the volume ratio, V_R, as a function of applied pressure, P, as shown below in equation (1).

$$\boldsymbol{V_R = m \ln P + b} \tag{1}$$

where,

$$V_R = \frac{V}{V_S}$$

P = applied pressure, MPa; V_R = volume ratio; V = volume of compact at pressure P, m^3; V_S = void free solid material volume, m^3

Later, Stewart (1938) verified Walker's model and characterized the compression of non-metallic powders, and particles of sulphur, ammonium and sodium chloride and trinitrotoluene (TNT). Bal'shin in 1938 (Denny, 2002) applied the concept of fluid mechanics and provided theoretical justification to the Walker's model. The Walker model has not been in significant use since its inception (Comoglu, 2007). Though, Adapa et al. (2002) attempted to use Walker model to study the compression behavior of fractionated alfalfa; however, good fit compared to other models was not obtained.

B.3.2 Jones Model

Similarly, Jones (1960) expressed the density-pressure data of compacted metal powder in the form of equation 2.

$$\ln \rho = \boldsymbol{m} \ln \boldsymbol{P} + \boldsymbol{b} \quad (2)$$

where, ρ is bulk density of compact powder mixture, kg/m^3; m and b are constants.

B.3.3 Heckel Model

Heckel (1961) considered the compaction of powders to be analogous to a first-order chemical reaction. The pores are the reactant for the densification of the bulk product. The "kinetics" of the process may be described as proportionality between the relative densities of a metal powder compact, ρ_f, and the applied pressure, P (Equation 3).

$$\ln \frac{1}{1-\rho_f} = \boldsymbol{mP} + \boldsymbol{b} \quad (3)$$

where,

$$b = ln\left(\frac{1}{1-\rho_0}\right)$$

$$\rho_f = \frac{\rho}{\rho_1 x_1 + \rho_2 x_2}$$

ρ_f = packing fraction or relative density of the material after particle rearrangement; ρ_0 = relative density of powder mixture, kg/m^3, ρ_1 and ρ_2 = particle density of components of the mixture, kg/m^3; x_1 and x_2 = mass fraction of components of the mixture.

The constants b and m are determined from the intercept and slope, respectively, of the extrapolated linear region of the plot of $ln(1/(1-\rho_f))$ vs P. A higher ρ_f value indicates that there is a higher volume reduction of the sample due to particle rearrangement. The constant m has been shown to be equal to the reciprocal of the mean yield pressure required to induce elastic deformation (York and Pilpel, 1973). A large m value (low yield pressure) indicates the onset of plastic deformation at relatively low pressure, thus, the material is more compressible. Depending on the property of material, some densify mostly by plastic deformation (e.g. fatty acids) while others densify by both particle rearrangement and plastic deformation (e.g. lactose powder). The Heckel model was also used to determine the compressibility of cellulose polymers by Shivanand and Sprockel (1992) and food material by Ollet et al. (1993).

B.3.4 Cooper-Eaton Model

Cooper-Eaton (1962) studied the compaction behavior of four ceramic powders. In each case they assumed that compression is attained by two nearly independent probabilistic processes, namely, the filling of voids having equal size as particles and filling of voids smaller than particles. Based on these assumptions, the following equation was given:

$$\frac{V_o - V}{V_o - V_S} = a_1 e^{-\frac{k_1}{P}} + a_2 e^{-\frac{k_2}{P}} \tag{4}$$

where, V_0 = volume of compact at zero pressure, m^3; a_1, a_2, k_1, and k_2 = Cooper-Eaton model constants.

The difficulty in practical use of the equation is the assignment of some physical significance to the constant parameters of this equation. In addition, another drawback of this model is its applicability to only one-component system (Comoglu, 2007)

B.3.5 Kawakita and Ludde Model

Kawakita and Ludde (1971) performed compression experiments and proposed an equation for compaction of powders based on observed relationship between pressure and volume (Equation 5).

$$\frac{P}{C} = \frac{1}{ab} + \frac{P}{a} \tag{5}$$

Where,

$$C = \frac{V_0 - V}{V_0}$$

C = degree of volume reduction or engineering strain; a and b = Kawakita-Ludde model constants related to characteristic of the powder.

The linear relationship between *P/C* and *P* allows the constants to be evaluated graphically. This compression equation holds true for soft and fluffy powders (Denny, 2002; Kawakita and Ludde, 1971), but particular attention must be paid on the measurement of the initial volume of the

powder. Any deviations from this expression are sometimes due to fluctuations in the measured value of V_0. The constant a is equal to the values of $C = C_\infty$ at infinitely large pressure P.

$$C_\infty = \frac{V_0 - V_\infty}{V_0}$$

Where, V_∞ = net volume of the powder, m^3.

It has been reported that the constant a is equal to the initial porosity of the sample, while constant $1/b$ is related to the failure stress in the case of piston compression (Mani et al., 2004).

Comoglu (2007) reported that the two most commonly used compression equations; Heckel (1961) and Kawakita and Ludde (1971), have not been proven to be successful in relating the densification behavior with the physical and mechanical properties of the materials. The Kawakita and Ludde (1971) equation works best for only limited range of materials, where as the Heckel (1961) equation produces curved plots (instead of linear plots). Even though these two equations appear very different, it has been shown mathematically that for pressure that are relatively low compared to the yield strength, the Kawakita and Ludde, and Heckel equations are identical in form.

B.3.6 Shapiro Model

Shapiro's model is only valid over the first two stages of compression process (Shapiro, 1993). Therefore, it will not be suitable to study compression behavior of agricultural biomasss grinds at high pressures; hence, it was not considered for further analysis. The Shapiro equation is as given below (Equation 6):

$$lnE = lnE_0 - kP - bP^{0.5} \quad (6)$$

where, E_0 = initial porosity; k and b are Shapiro constants.

B.3.7 Soonergaard Model (The log-exp-equation)

Sonnergaard (2001) proposed a log-exp-equation that simultaneously considered two processes: a logarithmic decrease in volume reduction by fragmentation and an exponential decay representing plastic deformation of powders (Equation 7).

$$V = V_1 - wlog(P) + V_0 exp(-P/P_m) \quad (7)$$

where, V_1 = volume at pressure 1 MPa; P_m = mean pressure, MPa; w is a constant.

Sonnergaard (2001) has suggested that his model provides better regression values compared to Cooper-Eaton model and Kawakita and Ludde model. However, the model is only suitable to describe compression of materials, when the investigation is performed at medium pressure range only (~50 MPa). Therefore, Sonnergaard model will not be suitable to study compression behavior of agricultural biomasss grinds at high pressures and hence, will not be considered for further analysis in the current study.

B.3.8 Panelli-Filho Model

A new compression equation (8) was proposed by Panelli-Filho (2001), given as:

$$\ln \frac{1}{1-\rho_r} = \boldsymbol{A}\sqrt{\boldsymbol{P}} + \boldsymbol{B} \tag{8}$$

where, ρ_r is the relative density of the compact; A is a parameter related to densification of the compact by particle deformation and B is a parameter related to powder density at the start of compression.

A majority of compression models applied to pharmaceutical and biomass materials have been discussed and reviewed in detail by Adapa et al. (2002), Denny (2002) and Mani et al. (2003). Mani et al. (2004) reported that among the different compression models, the Heckel and Cooper-Eaton models are still in use to study the compression mechanism of pharmaceutical and cellulosic materials. The Kawakita-Ludde model was proposed for soft and fluffy materials (Kawakita and Ludde, 1971). Adapa et al. (2002) and Tabil and Sokhansanj (1996) studied the applicability of these models for alfalfa pellets. They have concluded that the Cooper-Eaton, Heckel and Panelli-Filho models provided a better fit to the compression data. In the present study, five compression models were considered to determine the pressure-volume and pressure-density relationship to analyze the compression characteristics of barley, canola, oat and wheat straw namely: Jones (1960), Heckle (1961), Cooper-Eaton (1962), Kawakita-Ludde (1971), and Panelli-Filho (2001), models.

B.4 Materials and Methods

B.4.1 Agricultural Biomass

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for the experiments. The straw samples were acquired in small square bale form (typically having dimensions of 0.45 x 0.35 x 1.00 m) during the summer of 2008 from the Central Butte area of Saskatchewan, Canada.

All of the straw samples were manually chopped using a pair of scissors and subsequently ground using a forage grinder (Retsch GmbH, Model No. 70965, 5657 Haan, West Germany) with a screen opening size of 1.98 mm. The authors decided to use only one screen size of 1.98 mm based on the studies conducted by Adapa et al. (2004), which indicated that at this screen size, high quality fractionated alfalfa pellets were produced. In addition, literature review on the effect of grind size on compact density indicated the production of high density and quality pellets/briquettes at finer grind sizes (Kaliyan and Morey, 2006a and 2006b; Mani et al., 2002 and 2004).

The initial moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (wb), respectively. The moisture content of ground straw samples were raised to 10% (wb) by adding/sprinkling calculated amount of water and subsequently stored the samples in plastic bags in a cold room kept at 4^{o}C for a minimum of 72 h. The moisture content was determined using ASAE Standard S358.2 (ASAE Standards, 2006a), where oven drying of the samples was carried out at 103°C for 24 h. Only one moisture level of 10% (wb) was used and this was based upon literature review that at this moisture level high density and quality pellets/briquettes were produced from various straw and biomass (Hill and Pulkinen, 1988; Kaliyan and Morey, 2006b and 2007; Li and Liu, 2000; Mani et al., 2006a; Obernberger and Thek, 2004; Shaw and Tabil, 2007; Stevens, 1987).

B.4.2 Particle Size Analysis

Prior to pelleting experiments, the geometric mean particle size of ground agricultural straw samples at 10% moisture content (wb) was determined using ASAE Standard S319 (ASAE Standards, 2006b). For each test, a 100 g sample was placed on a stack of sieves arranged from

the largest to the smallest opening. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used to determine the geometric mean particle size using U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively). A 10 min sieve shaking time was considered appropriate due to the fluffy nature of the grinds. The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated in replicates of three for each straw samples.

B.4.3 Bulk and Particle Density

Bulk density of ground agricultural straw was determined by carefully filling a standard 0.5-L cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB) with sample. After filling every third portion of the container with ground straw sample, it was tapped on a wooden table for approximately 10 times to allow the material to settle down. After completely filling the container, excess material at the top was removed by moving a steel roller in a zig-zag pattern. The mass per unit volume gave the bulk density of the biomass in kg/m^3. A gas multi-pycnometer (QuantaChrome, Boynton Beach, FL) was used to determine the particle density of the ground straw by calculating the displaced volume of nitrogen gas by a known mass of material, following the method reported by Adapa et al. (2005). Three replicates for each sample were performed for both bulk and particle density measurements.

B.4.4 Experimental Set-up

A single pelleting unit (Adapa et al., 2006) having a close fit plunger die assembly was used to study the compression characteristics of fractionated alfalfa grinds (Adapa et al., 2002). The cylindrical die was 135.3 mm long and 6.35 mm in diameter. Thermal compound (Wakefield Engineering Inc., Wakefield, MA) was coated on the outer surface of the die prior to wrapping the outer surface with copper shim stock. A dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, IL) was then wound evenly around the shim stock to provide the necessary heat. One type-T thermocouple, connected to the outer surface of the cylinder, was linked to a temperature controller to regulate the power input to the heater, thus allowing temperature control of the cylinder. Another type-T thermocouple was also connected to the outer cylinder wall, allowed verification of the cylinder temperature via a digital thermocouple reader (Shaw, 2008). The pellet die was fitted on a stainless steel base having a hole matching

its outer diameter. This gave stability and allowed the plunger to move straight down with no lateral movement. The plunger was attached to the upper moving crosshead of the Instron Model 1011 testing machine (Instron Corp., Canton, MA).

B.4.5 Compression Test

The pelleting unit was used to make a single pellet in one stroke of the plunger from ground straw samples. The pellet die was maintained at a temperature of 95±1^{o}C in order to simulate frictional heating during commercial pelleting operation (Adapa et al., 2006 and Mani et al., 2006b). The mass of samples used for making pellets varied between 0.5 and 0.7 g. Compressive force was applied using the Instron Model 1011 testing machine fitted with a 5000 N load cell and a 6.3 mm diameter plunger. Four preset loads of 1000, 2000, 3000 and 4400 N corresponding to pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were used to compress samples in the die. The crosshead speed of the Instron testing machine was set at 50 mm/min. After compression, the plunger was retained in place for 30 s once the preset load was attained in order to avoid spring-back effect of biomass grinds (Adapa et al., 2006 and Mani et al., 2006b). Later, the base plate was removed and the pellet was ejected / extruded from the single pelleter by using the plunger.

B.4.6 Statistical Analysis

The experiments were set up as completely random experimental design with 10 replications and two-variables (straw and pressure) factorial design. The volume and density were the dependent variables, while pressure was the independent variable. The mass, length and diameter of pellets were measured to determine the pellet volume (m^3) and density (kg/m^3). Ten replicates (pellets) were made using each ground straw samples. The model parameters were estimated using MS Excel software and SAS software for Windows (version 8.2) (SAS Institute, 1999). Model parameters for Cooper-Eaton model were determined using PROC NLIN program in the SAS software package. In order to further understand and explain the experimental variables and their interactions, the SAS general linear model (GLM) for completely randomized design (CRD) procedure was used and the Student-Neuman-Keuls test (SNK) was performed. SNK determines the difference between any two treatment means at 5% level of significance (SAS Manual, SAS Institute, 1999).

B.5 Results and Discussion

B.5.1 Physical Properties

The geometric mean particle size, bulk and particle densities of ground barley, canola, oat and wheat straw at 10% moisture content (wb) are listed in Table B.1. The SNK test indicated that the geometric mean particle size of oat straw (0.347 mm) was significantly smaller ($P < 0.05$) than the other straw samples. The mean bulk density of ground canola straw was highest (273 kg/m^3); however, the bulk densities for all the straw samples were not statistically different ($P > 0.05$). It was observed that ground wheat and barley straw have the highest (1585 kg/m^3) and lowest (1484 kg/m^3) mean particle densities, respectively. The mean particle density of barley, canola and oat straw were statistically similar, while the mean particle densities of canola, oat and wheat straw were not significantly different.

Table B.1: Geometric mean particle size, bulk and particles densities for four ground agricultural straw samples at 10% moisture content (wb).

Biomass	Geometric Mean Particle Size (mm)	Moisture content 10% (w.b.)	
		Bulk density (kg/m^3)	Particle density (kg/m^3)
Barley Straw	0.384 ± 0.003 a γ†‡	261 ± 02 a	1484 ± 03 a
Canola Straw	0.391 ± 0.017 a	273 ± 11 a	1551 ± 47 ab
Oat Straw	0.347 ± 0.003 b	268 ± 04 a	1523 ± 15 ab
Wheat Straw	0.398 ± 0.006 a	269 ± 09 a	1585 ± 46 b

γ3 replicates; †95% confidence interval; ‡ Student-Neuman-Keuls test at 5% level of significance

B.5.2 Compression Test

Table B.2 shows the effect of applied pressure on pellet density and volume for four ground agricultural straws. The actual compressive force recorded by the Instron machine was slightly higher than the preset values (applied load). The recorded compressive forces had higher variability at higher preset loads due to the inertia of crosshead and limitations in testing machine

control. Two SNK analyses were performed on the collected data. In the first SNK analysis, treatment means for the same straw sample at different pressures were compared and the differences were shown by designations of the lower case letters a, b and c. The second SNK analysis was performed to determine the difference in treatment means for the four straw samples at the same pressure with the upper case letters D and E used to show the difference.

Figure B.2 shows that the pellet density for all four agricultural straw samples increased with an increase in pressure. The mean densities of barley, canola, oat and wheat straw pellets increased from 907 to 977 kg/m^3, 823 to 1003 kg/m^3, 849 to 1011 kg/m^3 and 813 to 924 kg/m^3, respectively. For barley and wheat straw pellets, the increase in density was significant ($P < 0.05$) for an increase of pressure from 31.6 to 63.2 MPa (Table B.2). Table B.2 also indicates that for canola and oat straw pellets, the increase in density were significant ($P < 0.05$) for an increase in applied pressure from 31.6 to 94.7 MPa. Application of higher pressure (> 94.7 MPa) did not affect the compact density as the pellets approached their respective particle densities. The wheat straw pellets has been an exception as although it has larger geometric mean particle size and particle densities (Table B.1), its density reached a maximum value at a pressure of 63.2 MPa. This could possibly be attributed to the lower total protein and lignin contents as compared to other straw material, which resulted in a better pellet.

At pressures of 31.6 and 63.2 MPa, the density of pellet from barley straw was significantly higher than the densities of other agricultural straw pellets (Table B.2), which could be attributed to a combination of lowest particle density (1484 kg/m^3) and geometric mean particles size. However, at pressures of 94.7 and 138.9 MPa, the density of pellets from wheat straw was significantly lower than the densities of other agricultural straw pellets. This could be due to the fact that wheat straw had both highest particles density (1585 kg/m^3) and geometric mean particle size.

Generally, at any particular pressure, the density of pellets was highest for oat straw followed by barley, canola and wheat straw in decreasing order (Table B.2). This could be attributed to the geometric mean particle size for oat straw (0.347 mm), which was followed by barley (0.384), canola (0.391) and wheat (0.398) straw in increasing order. The finer grind size has been reported to produce denser pellets (Kaliyan and Morey, 2006a and 2006b; Mani et al., 2002 and 2004).

Table B.2: Observed compressive forces; measured pellet mass, diameter and length; and calculated volume and density data for selected agricultural biomass.

Biomass	Applied Load$^{\Theta}$ (N)	Compressive Force$^{\Theta\Theta}$ (N)	Pellet Mass (g)	Pellet Diameter (mm)	Pellet Length (mm)	Pressure (MPa)	Δ_p* (kg/m^3)	Δ_t** (kg/m^3)	Δ_b*** (kg/m^3)	Volume (mm^3)	
										V^{+}	Vs^{++}
Barley	1000	1224 ± 42*†	0.58 ± 0.04	6.46 ± 0.02	19.55 ± 1.37	30.5 ± 0.2	907 ± 31 aD‡	1484 ± 03	261 ± 02	642 ± 46	392 ± 24
Straw	2000	2339 ± 53	0.62 ± 0.03	6.48 ± 0.01	19.15 ± 1.15	60.6 ± 0.3	978 ± 14 bD			632 ± 38	416 ± 22
	3000	3395 ± 50	0.59 ± 0.05	6.47 ± 0.01	18.24 ± 1.38	91.2 ± 0.3	988 ± 26 bD			600 ± 45	399 ± 34
	4400	4725 ± 63	0.58 ± 0.05	6.47 ± 0.01	18.17 ± 1.32	133.8 ± 0.6	977 ± 38 bD			597 ± 45	394 ± 35
Canola	1000	1214 ± 41	0.65 ± 0.06	6.49 ± 0.03	24.04 ± 2.24	30.2 ± 0.3	823 ± 73 aE	1551 ± 47	273 ± 11	796 ± 74	421 ± 36
Straw	2000	2324 ± 36	0.68 ± 0.04	6.47 ± 0.02	22.15 ± 1.49	60.9 ± 0.3	934 ± 21 bE			728 ± 49	438 ± 25
	3000	3381 ± 42	0.68 ± 0.02	6.49 ± 0.01	21.06 ± 0.82	90.9 ± 0.4	980 ± 17 cD			695 ± 27	439 ± 14
	4400	4569 ± 31	0.70 ± 0.04	6.47 ± 0.01	21.19 ± 0.98	133.7 ± 0.4	1003 ± 21 cD			698 ± 32	452 ± 26
Oat	1000	1211 ± 57	0.57 ± 0.03	6.49 ± 0.02	20.25 ± 1.09	30.2 ± 0.2	849 ± 22 aE	1523 ± 15	268 ± 04	669 ± 37	373 ± 20
Straw	2000	2364 ± 33	0.58 ± 0.04	6.49 ± 0.01	18.55 ± 0.75	60.5 ± 0.3	937 ± 56 bE			614 ± 24	378 ± 26
	3000	3438 ± 51	0.60 ± 0.05	6.47 ± 0.01	18.43 ± 0.72	91.4 ± 0.3	991 ± 63 cD			605 ± 23	394 ± 34
	4400	4625 ± 21	0.61 ± 0.04	6.47 ± 0.01	18.48 ± 0.93	133.7 ± 0.6	1011 ± 54 cD			608 ± 31	403 ± 29
Wheat	1000	1210 ± 49	0.52 ± 0.03	6.49 ± 0.04	19.37 ± 1.79	30.3 ± 0.4	813 ± 55 aE	1585 ± 46	269 ± 09	640 ± 63	327 ± 20
Straw	2000	2383 ± 50	0.56 ± 0.06	6.48 ± 0.02	18.30 ± 1.75	60.7 ± 0.4	929 ± 30 bE			603 ± 57	353 ± 35
	3000	3333 ± 90	0.54 ± 0.05	6.48 ± 0.01	17.45 ± 1.56	91.1 ± 0.4	931 ± 34 bE			575 ± 52	338 ± 33
	4400	4687 ± 41	0.62 ± 0.03	6.48 ± 0.01	20.51 ± 0.99	133.4 ± 0.4	924 ± 23			676 ± 32	394 ± 20

$^{\Theta}$ Preset compressive load on the Instron for forming pellets

$^{\Theta\Theta}$ Actual force registered by the Instron due to inertia

$^{*}\Delta_p$ Pellet density

$^{**}\Delta_t$ Particle density of the ground agricultural biomass, n = 3

$^{***}\Delta_b$ Bulk density of the ground agricultural biomass, n = 3

$^{+}$V Volume of the compact at pressure P

$^{++}$Vs Void-free solid material volume

†95% confidence interval

‡ Student-Neuman-Keuls test at 5% level of significance

Number of replicates for each run of compaction, n = 10

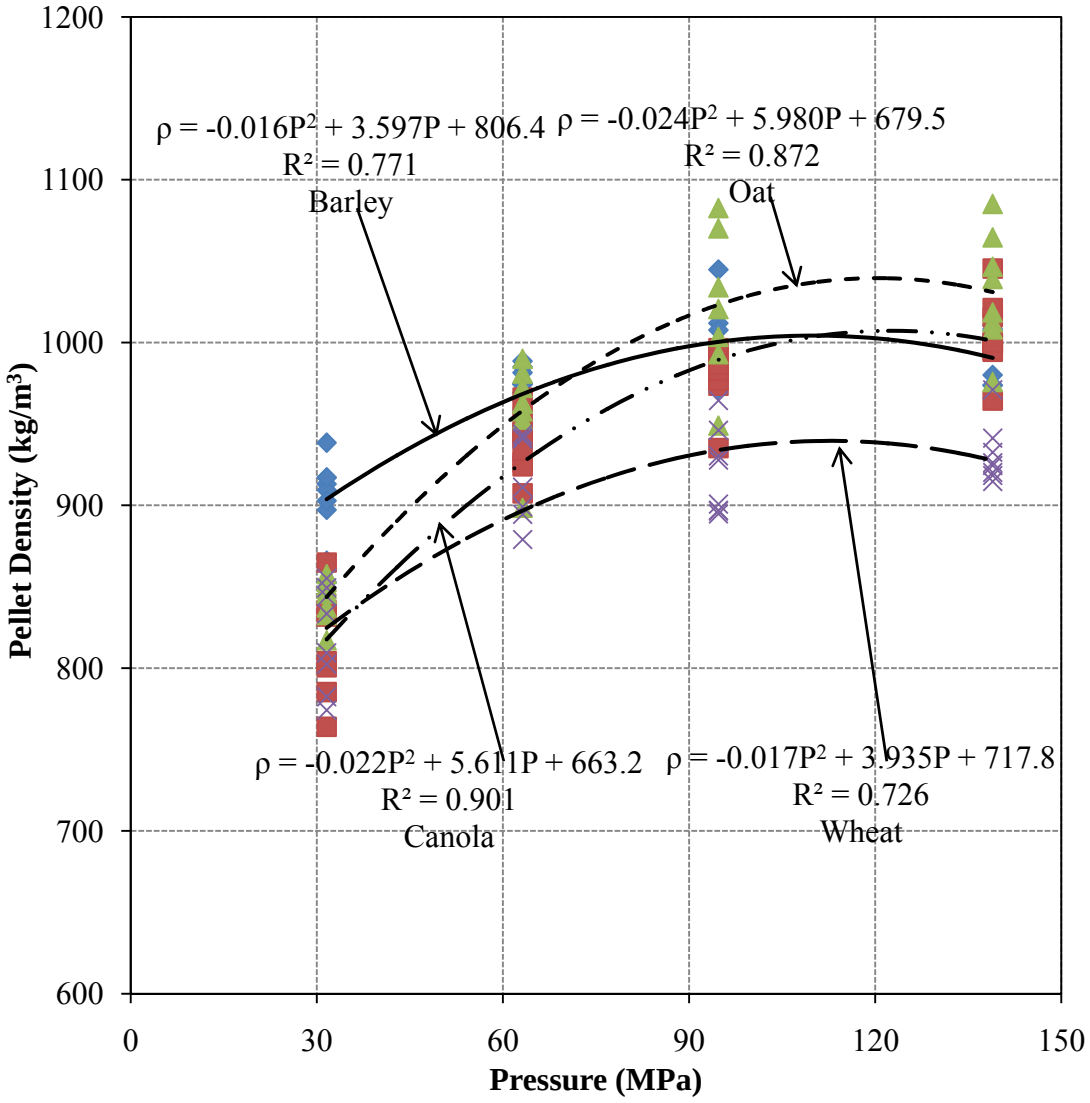


Figure B.2: Density of pellets and their empirical equations for four agricultural straw samples at four pressure levels

B.5.3 Fitting Compression Models to Pressure, Density and Volume Data

Five compression models were fitted to the pressure-volume and pressure-density data to analyze the compression characteristics of barley, canola, oat and wheat straw. Tables B.3 to B.7 presents the parameters obtained after curve fitting Jones (1960), Heckle (1961), Cooper-Eaton (1962), Kawakita-Ludde (1971), and Panelli-Filho (2001) models, respectively.

Jones (1960) derived a linear equation, which expressed the logarithmic value of density as a function of the logarithmic pressure. Low R^2 values were obtained when the Jones model was fitted to the pressure-density data (Table B.3). The R^2 values for barley, canola, oat and wheat straw were 0.42, 0.68, 0.63 and 0.46, respectively.

Similar to Jones model (1960), the Heckel model (1961) was unable to explain the trend in variation of pressure and density data (Table B.4). However, the value of constant *m* provided valuable information about the onset of plastic deformation of the ground straw at relatively low pressure, thus, indicating that the material is more compressible. Higher *m* values for canola and oat straw (0.002) were observed as compared to barley and wheat straw (0.001) indicating they are more compressible. The R^2 values obtained for barley, canola, oat and wheat straw were 0.42, 0.71, 0.62 and 0.47, respectively.

Table B.5 represents the parameters obtained when the Cooper-Eaton model (1962) was fitted to the experimental data. The dimensionless coefficients, a_1 and a_2 represent the densification of powdered material by particle rearrangement and deformation, respectively. If the sum of coefficients ($a_1 + a_2$) is less than unity, it is an indication that other process must become operative before complete compaction is achieved. The a_1 values for four selected agricultural biomass were higher than a_2 values, which indicates that material densified easily by particle rearrangement. The sum of coefficients ($a_1 + a_2$) for barley and oat straw were near and below unity, which indicates that the samples almost reached their theoretical density. While the sum of coefficients for canola and wheat straw were observed to be above unity. The phenomenon of having sum of coefficient more than unity was also observed by Adapa et al. (2002), and Shivanand and Sprockel (1992), which implies that the densification could not be fully attributed to the two mechanisms of compression assumed by Cooper-Eaton (1962). The R^2 values obtained for barley, canola, oat and wheat straw were 0.52, 0.72, 0.64 and 0.64, respectively.

It has been observed that the Kawakita-Ludde model (Table B.6) provided the best fit scenario having R^2 values of 0.99 for all biomass samples (Figure B.3). All other models were unable to sufficiently describe the compression behavior of selected agricultural biomass. In Kawakita-Ludde model, the constant *a* represents the initial porosity of the sample. Table 6 shows that the oat straw had the highest initial porosity value (0.751) followed by the canola (0.749), barley (0.738) and wheat (0.720) straw. The porosity value for oat straw can be related to its lowest

geometric mean particle size (0.347 mm) while having similar bulk densities (268 kg/m^3) as the other samples (Table B.1). The parameter *1/b* indicates the yield strength or failure stress of the compact. The highest value of failure stress (3.801) was observed for ground canola straw sample followed by oat (3.149), wheat (1.727) and barley (0.776) straw.

Panelli-Filho model (2001) was unable to provide a better fit to the pressure-density data. The R^2 values obtained for barley, canola, oat and wheat straw were 0.36, 0.74, 0.57 and 0.40, respectively (Table B.7).

Table B.3: Jones Model $\ln \rho = \boldsymbol{m} \ln \boldsymbol{P} + \boldsymbol{b}$

Biomass	Constants		R^2 Values	SSE
	m	b		
Barley Straw	0.052	6.643	0.42	0.046
Canola Straw	0.138	6.243	0.71	0.094
Oat Straw	0.120	6.333	0.62	0.108
Wheat Straw	0.089	6.418	0.47	0.109

Table B.4: Heckel Model $\ln \frac{1}{1-\rho_f} = \boldsymbol{mP} + \boldsymbol{b}$

Biomass	Constants		R^2 Values	SSE
	m	b		
Barley Straw	0.001	0.959	0.31	6.696
Canola Straw	0.002	0.724	0.70	5.102
Oat Straw	0.002	0.771	0.55	6.197
Wheat Straw	0.001	0.740	0.34	3.393

Table B.5: Cooper – Eaton Model $\frac{V_0 - V}{V_0 - Vs} = a_1 e^{-\frac{k_1}{P}} + a_2 e^{-\frac{k_2}{P}}$

Biomass	Constants				R^2 Values	SSE
	a_1	a_2	k_1	k_2		
Barley Straw	0.7025	0.2000	1.3025	1.3024	0.52	0.004
Canola Straw	1.8141	-0.9117	-1.6542	-6.0377	0.72	0.014
Oat Straw	0.8958	0.0202	4.5734	-31.7373	0.64	0.012
Wheat Straw	1.4503	-0.6091	-11.3827	-23.3329	0.64	0.011

Table B.6: Kawakita-Ludde Model $\frac{\boldsymbol{P}}{\boldsymbol{C}} = \frac{1}{\boldsymbol{ab}} + \frac{\boldsymbol{P}}{\boldsymbol{a}}$

Biomass	Constants		R^2 Values	SSE
	a	1/b		
Barley Straw	0.738	0.776	0.99	100.33
Canola Straw	0.749	3.801	0.99	81.58
Oat Straw	0.751	3.149	0.99	272.37
Wheat Straw	0.720	1.727	0.99	144.13

Table B.7: Panelli – Filho Model $\ln \frac{1}{1-\rho_r} = \boldsymbol{A}\sqrt{\boldsymbol{P}} + \boldsymbol{B}$

Biomass	Constants		R^2 Values	SSE
	A	B		
Barley Straw	0.020	0.866	0.36	0.162
Canola Straw	0.045	0.530	0.74	0.153
Oat Straw	0.046	0.576	0.57	0.332
Wheat Straw	0.023	0.634	0.40	0.175

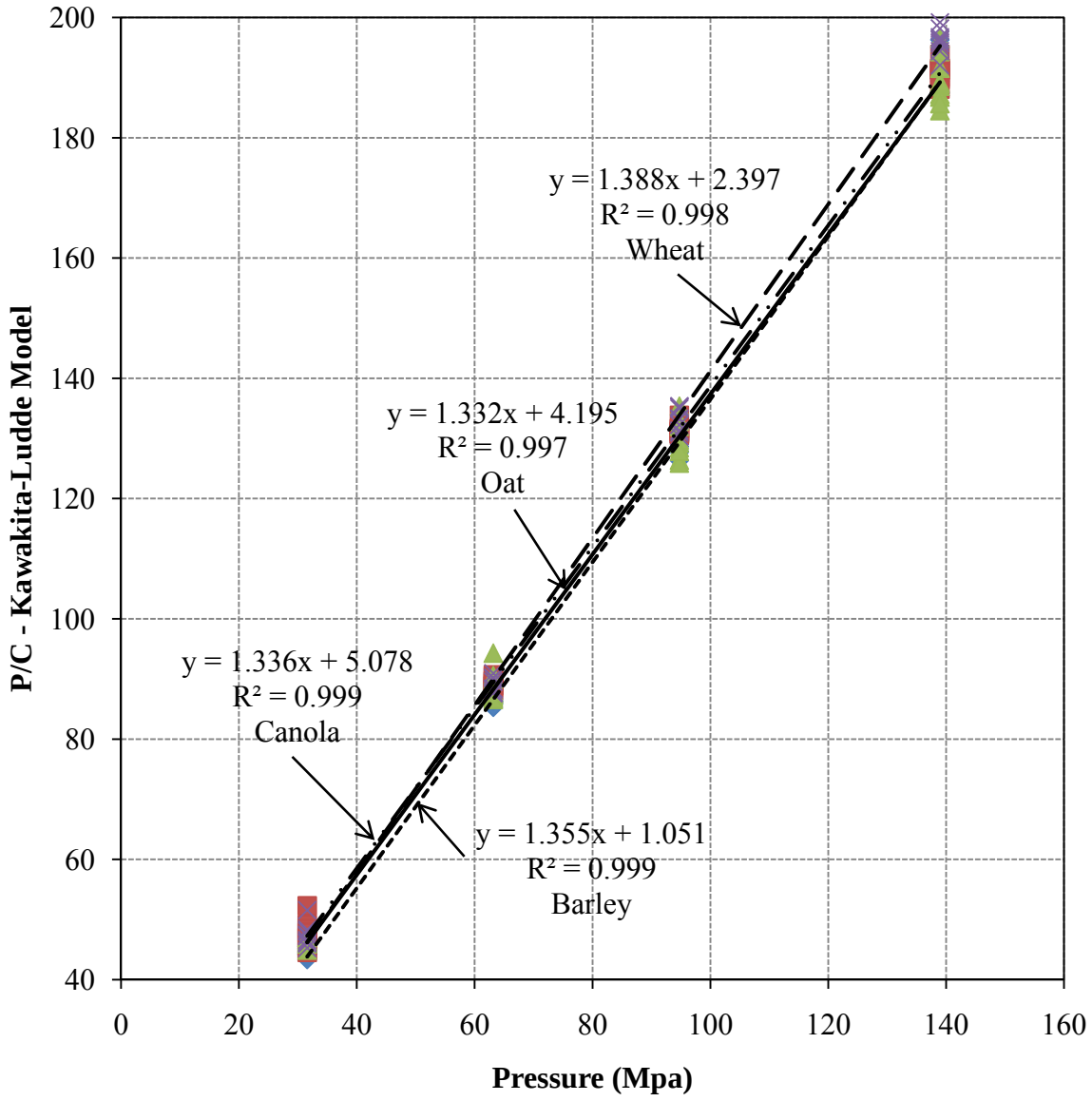


Figure B.3: Kawakita-Ludde model fitted to the experimental data obtained from densification of selected agricultural biomass.

B.6 Summary

A review of various existing compression models was successfully performed. In addition, the compaction characteristics of ground barley, canola, oat and wheat straw samples at 10% moisture content (wb) and grind size of 1.98 mm was studied by subjecting the samples to four pressure levels of 31.6, 63.2, 94.7 and 138.9 MPa. Five models, namely: Jones (1960), Heckle

(1961), Cooper-Eaton (1962), Kawakita-Ludde (1971), and Panelli-Filho (2001) models were fitted to the pressure-density-volume data. The Kawakita-Ludde model provided an excellent fit having R^2 values of 0.99 for four selected agricultural straw samples. It was also concluded that the ground oat and canola straw had the highest level of porosity and failure stress, respectively. The parameters of Cooper-Eaton model indicated that the ground straw samples were densified easily by the particles rearrangement method and Jones model indicated that canola and oat straw were more compressible as compared to barley and wheat straw.

Appendix C

C. Preliminary Compaction Experiments on Non-Treated Agricultural Straw Grinds (Chapter 5)

A similar version of this Appendix has been published with the journal Biosystems Engineering:

- Adapa, P.K., L.G. Tabil and G.J. Schoenau. 2009. Compression characteristics of selected ground agricultural biomass. *Agricultural Engineering International: the CIGR Ejournal*, Manuscript 1347, XI(June): 1-19.

C.1 Abstract

Agricultural biomass has the potential to be used as feedstock for biofuel production. However, crop residue after harvest must be gathered, processed and densified in order to facilitate efficient handling, transportation and usage. In this study compacts were prepared by densifying material against a base plate (representing the specific energy required to overcome friction within the straw grinds) as opposed to the process that occurs in a commercial operation where compacts are formed due to back-pressure effect in the die. Densification was measured using four selected biomass samples (barley, canola (oilseed rape), oat and wheat straw) at 10% moisture content (wb) and 1.98 mm grinder screen size using a compaction apparatus which applied four pressure levels of 31.6, 63.2, 94.7 and 138.9 MPa. The specific energy required to extrude the compact was measured; this will closely emulate the specific energy required to overcome the friction between the ground straw and die. The mean densities of barley, canola, oat and wheat straw compacts ranged from 907±31 to 988±26 kg/m^3, 823±73 to 1003±21 kg/m^3, 849±22 to 1011±54 kg/m^3 and 813±55 to 924±23 kg/m^3, respectively; while the mean total

specific energy for compaction of grinds ranged from 3.69±0.28 to 9.29±0.39 MJ/t, 3.31±0.82 to 9.44±0.33 MJ/t, 5.25±0.42 to 9.57±0.83 MJ/t and 3.59±0.44 to 7.16±0.40 MJ/t, respectively. Best predictor equations having highest coefficient of determination values (R^2) and standard error of estimate or root mean square error were determined for both compact density and total specific energy required to compress the ground straw samples. The resulting R^2 for pellet density from barley, canola, oat and wheat straw were 0.56, 0.79, 0.67 and 0.62, respectively, and for total specific energy the values of R^2 were 0.94, 0.96, 0.90 and 0.92, respectively.

C.2 Introduction

Agricultural biomass residues have the potential for the sustainable production of bio-fuels and to offset greenhouse gas emissions (Campbell et al., 2002; Sokhansanj et al., 2006). The straw and agricultural residues existing in the waste streams from commercial crop processing plants have little inherent value and have traditionally constituted a disposal problem. In fact, these residues represent an abundant, inexpensive and readily available source of renewable lignocellulosic biomass (Liu et al., 2005). New methodologies need to be developed to process the biomass making it suitable feedstock for bio-fuel production. In addition, some of the barriers to the economic use of agricultural crop residue are the variable quality of the residue, the cost of collection, and problems in transportation and storage (Bowyer and Stockmann, 2001; Sokhansanj et al., 2006).

In order to reduce industry's operational cost as well as to meet the requirement of raw material for biofuel production, biomass must be processed and handled in an efficient manner. Due to its high moisture content, irregular shape and sizes, and low bulk density, biomass is very difficult to handle, transport, store, and utilise in its original form (Sokhansanj et al., 2005). Densification of biomass into durable compacts is an effective solution to these problems and it can reduce material waste. Densification can increase the bulk density of biomass from an initial bulk density of 40-200 kg/m^3 to a final compact density of 600-1200 kg/m^3 (Adapa et al., 2007a; Holley, 1983; Mani et al., 2003; McMullen et al., 2005; Obernberger and Thek, 2004). Because of their uniform shape and size, densified products may be easily handled using standard handling and storage equipment, and they can be easily adopted in direct-combustion or co-firing

with coal, gasification, pyrolysis, and in other biomass-based conversions (Kaliyan and Morey, 2006a). Upon densification, many agricultural biomass materials, especially those from straw and stover, result in a poorly formed pellets or compacts that are more often dusty, difficult to handle and costly to manufacture. This is caused by lack of complete understanding on the natural binding characteristics of the components that make up biomass (Sokhansanj et al., 2005).

High quality compacts can be produced by the control of the manufacturing operations and biomass physical and chemical characteristics. Biomass grinds vary in their response to the compression forces during pelleting. To a great extent, the quality of manufactured compacts depends on the physical forces that bond the particles together (Adapa et al., 2002). To customise and manufacture high quality products that can withstand various forces during transportation and handling, it is essential to predict desirable and dependent quality parameters (density and durability) with respect to various independent variables (moisture content and grind size) (Adapa et al., 2007a). In addition, specific energy requirements of manufacturing biomass compacts should be established, which can assist in determining the economic viability of densification process.

C.2.1 Effect of Moisture Content on Compact Density

The moisture in biomass both acts as a facilitator of natural binding agents and a lubricant (Kaliyan and Morey, 2006a). Hill and Pulkinen (1988) recommended an optimum moisture content of 8 to 9% (wb) for producing high quality alfalfa pellets in a pellet mill. Generally, moisture contents of 11 to 12% (wb) are used for wheat- and corn-based feed pelleting (Stevens, 1987). Li and Liu (2000) concluded that good quality wood logs can be produced with initial moisture contents of 6 to 12% (wb); however, the optimum moisture content is around 8% (wb). According to Obernberger and Thek (2004), production of high quality pellets is possible only if the moisture content of the feed is between 8 and 12% (wb). Moisture contents above or below this range would lead to lower quality pellets.

Kaliyan and Morey (2006b) observed no significant difference in briquette densities for 10 and 15% moisture contents at an applied pressure of 100 MPa for corn stover; however, the densities decreased with an increase in moisture from 10 to 15% at a pressure of 150 MPa. An increase in

the moisture content from 10 to 15% resulted in 30 to 40% decrease in compact densities of switchgrass. A similar trend of decrease in density with increasing moisture levels was reported by Chancellor (1962) for alfalfa hay and by Mani et al. (2002) for pellets made from wheat straw, barley straw, corn stover, and switchgrass. Mani et al. (2006a) observed maximum briquette density of about 950 kg/m^3 for corn stover at 5-10% moisture content. They also observed that a combination of high moisture (15%) and pressure (15 MPa) had a negative effect on briquette density. Smith et al. (1977) reported similar results for wheat straw. Grover and Mishra (1996) also recommended low moisture content in the range of 8-10% for biomass materials to produce high quality briquettes.

Mani et al. (2006b) and Gustafson and Kjelgaard (1963) studied the compaction of agricultural biomass for a wide range of moisture (28–44% (wb)) and found that the density of the product decreased as moisture content increased. Rehkugler and Buchele (1969) reported that there was a reduction in relaxed density of pellet for moisture content ranging between 6% and 25% (wb). Kaliyan and Morey (2007) observed that for both corn stover and switchgrass, the bulk density of compacts decreased with an increase of moisture content from 7 to 15% and 9 to 20%, respectively. In addition, they concluded that grinds at moisture content of 10% (wb) produced good quality compacts. Shaw (2008) observed that at lower loads, the compact density was higher at 15% (wb); however, as the load was increased (from 1000 N to 4000 N), the compacts made from 9% (wb) moisture produced denser compacts. Shaw and Tabil (2007) also reported similar results and concluded that lower moisture materials produce denser compacts.

C.2.2 Effect of Grind Size on Compact Density

Kaliyan and Morey (2006a) indicated that generally, the finer the grind, the higher the quality of compact. Fine particles readily absorb moisture than large particles, and therefore, undergo a higher degree of conditioning. Also, large particles are fissure points that cause cracks and fractures in compacts (MacBain, 1966).

Mani et al. (2002 and 2004a) reported an increase in pellet densities from 5 to 16% when pelleting corn stover grind obtained from the hammer mill screen sizes of 3.2, 1.6 and 0.8 mm. Similar results were reported by Kaliyan and Morey (2006b) of an increase in briquette densities from 5 to 10% when the geometric mean particle size of corn stover grinds decreased from 0.80

to 0.66 mm. For switchgrass, reducing the geometric mean particle size from 0.64 to 0.56 mm did not show significant impact on the briquette density (Kaliyan and Morey 2006b). The observations have been echoed by Mani et al. (2002) who were unable to show any trend in variation in switchgrass pellet densities made with grinds having geometric mean particle size in the range of 0.25 to 0.46 mm.

C.2.3 Compression and Extrusion Specific Energy

Energy requirements for densification of biomass depend primarily upon the applied pressure and moisture content of the material. It also depends on the physical properties of the material and the method of compaction (Mani et al., 2004a). During compression, high levels of friction are encountered as forage extrudes through the die in addition to the resistance encountered in compressing the forage (Hann and Harrison, 1976).

Mani et al. (2006a) successfully densified corn stover into dense briquettes having density of 650-950 kg/m^3 and the specific energy required to compress and extrude corn stover was in the range of 12-30 MJ/t. The extrusion (frictional) energy required to overcome the skin friction was roughly half of the total energy. Mewes (1959) showed that roughly 40% of the total applied energy was used to compress the materials (straw and hay) and the remaining 60% was used to overcome friction. Bellinger and McColly (1961) reported that the pushing energy for circular dies was up to 2 MJ/t for alfalfa which was about 10-15% of the total applied energy. Thus, a large fraction of the energy required to densify biomass is used to overcome friction in pushing the densified product out of the die.

Abd-Elrahim et al. (1981) reported a specific energy consumption of 7.2 MJ/t for compression of cotton stalks in circular dies. The compression of barley straw in a circular die required a specific energy consumption of 5-25 MJ/t depending on the compact density (O'Dogherty and Wheeler, 1984). Faborode and O'Callaghan (1987) studied the energy requirement for compression of fibrous agricultural materials. They reported that chopped barley straw at 8.3% (wb) moisture content consumed 28-31 MJ/t of energy, while un-chopped material consumed 18-27 MJ/t. Kaliyan and Morey (2006b) reported that at pressure of 150 MPa, 10% moisture content and a preheat of 100^{o}C, decreasing the particle size of corn stover grind from 0.8 to 0.66 mm did not result in significant change in specific energy consumption from 189 MJ/t. Whereas

for switchgrass briquetting, decreasing the particle size from 0.64 to 0.56 mm slightly decreased the specific energy consumption from 189 to 187 MJ/t. Shaw (2008) reported that between 95 and 99% of the total specific energy was required to compress the grinds, whereas between 1 and 5% of the total specific energy was required to extrude the compact in single compact tests. Shaw (2008) also reported that the mean values of specific compression energy ranged from 7.2 (pretreated wheat straw using steam explosion) to 39.1 MJ/t (wheat straw).

In this study, we have explored the effect of various pressure levels on density and specific energy requirements for compacting selected ground agricultural biomass (barley, canola, oat and wheat straw). Some previous work had been reported by Mani et al. (2006a and 2006b) on mechanical properties of ground barley and wheat straw and by Shaw (2008) on ground wheat straw as a feedstock for biofuel industry. However, detailed study on density and specific energy statistical models had not been reported. In addition, the authors were unable to find any literature on densification of canola and oat straw. Therefore, the objective of this study was to study the effect of pressure on the densification characteristics of barley, canola, oat and wheat straw grinds.

C.3 Materials and Methods

C.3.1 Agricultural Biomass

Four types of agricultural biomass (barley, canola, oat and wheat straw) were used for the experiments. The straw samples were acquired in small square bale form (typically having dimensions of 0.45 x 0.35 x 1.00 m) during the summer of 2008 from the Central Butte area of Saskatchewan, Canada.

All of the straw samples were manually chopped using a pair of scissors and subsequently ground using a forage grinder (Retsch GmbH, Model No. 70965, 5657 Haan, West Germany) with a screen opening size of 1.98 mm. The authors decided to use only one screen size of 1.98 mm based on the studies conducted by Adapa et al. (2004), which indicated that at this screen size, high quality fractionated alfalfa compacts were produced. In addition, a literature review on the effect of grind size on compact density indicated the production of high density and

quality compacts/briquettes at finer grind sizes (Kaliyan and Morey, 2006a and 2006b; Mani et al., 2002 and 2004a).

The initial moisture contents of ground barley, canola, oat and wheat straw were 6.7, 6.7, 5.3 and 4.0% (wb), respectively. The moisture content of ground straw was raised to 10% (wb) by adding/sprinkling a calculated amount of water. The samples were subsequently stored in plastic bags and kept in a cold room at 4^{o}C for a minimum of 72 h. The moisture content was determined using ASAE Standard S358.2 (ASAE, 2006a), where oven drying of the samples was carried out at 103°C for 24 h. Only one moisture level of 10% (wb) was used and this was based upon literature review that at this moisture level, high density and quality pellets/briquettes were produced from various straw and biomass (Hill and Pulkinen, 1988; Kaliyan and Morey, 2006b and 2007; Li and Liu, 2000; Mani et al., 2006a; Obernberger and Thek, 2004; Shaw and Tabil, 2007; Stevens, 1987).

C.3.2 Particle Size Analysis

Prior to densification experiments, the geometric mean particle diameter of ground agricultural straw samples at 10% moisture content (wb) was determined using ASAE Standard S319 (ASAE, 2006b). For each test, a 100 g sample was placed on a stack of sieves arranged from the largest to the smallest opening. A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH, USA) was used to determine the geometric mean particle size using U.S. sieve numbers 16, 20, 30, 50, 70 and 100 (sieve opening sizes: 1.190, 0.841, 0.595, 0.297, 0.210 and 0.149 mm, respectively). A 10 min sieve shaking time was used as suggested in the ASAE Standard S319. The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated in replicates of three for each straw samples.

C.3.3 Bulk and Particle Density

Bulk density of ground agricultural straw was determined by carefully filling a standard 0.5 l cylindrical container (SWA951, Superior Scale Co. Ltd., Winnipeg, MB, Canada) with sample. After filling every third portion of the container with ground straw sample, it was tapped on a wooden table for approximately 10 times to allow the material to settle down. After completely filling the container, excess material at the top was removed by moving a steel roller in a zig-zag

pattern. The mass per unit volume gave the bulk density of the biomass in kg m^{-3}. A gas multi-pycnometer (QuantaChrome, Boynton Beach, FL, USA) was used to determine the particle density of the ground straw by calculating the displaced volume of nitrogen gas by a known mass of material, following the method reported by Adapa et al. (2005). Three replicates for each sample were performed for both bulk and particle density measurements.

C.3.4 Chemical Composition

The chemical composition analysis of barley, canola, oat and wheat straw was performed in duplicates by the SunWest Food Laboratory Ltd., Saskatoon, SK, Canada. Protein, fat, starch, lignin, acid detergent fibre (ADF), neutral detergent fibre (NDF) and total ash contents were determined. The protein content of the biomass was determined using the AOAC standard method (AOAC, 2001), where the nitrogen content was multiplied by a factor 6.25. Crude fat was determined using AOCS standard method Am2-93 (AOCS, 1999). Total starch content was measured using AOAC standard method 996.11 (AOAC, 1998). Lignin and ADF were determined using AOAC standard method 973.18 (AOAC, 1990a), whereas NDF was determined using AOAC standard method 992.16 (AOAC, 1990b). The total ash content was determined using AOAC standard method 942.05 (AOAC, 1990c). Cellulose percentage is calculated indirectly from percentage acid detergent fibre (ADF) and lignin (%ADF minus %lignin) (Mani et al., 2006b). Hemicellulose percentage is calculated indirectly from percentage neutral detergent fibre (NDF) and ADF (% NDF minus %ADF) (Mani et al., 2006b).

C.3.5 Apparatus

A compaction apparatus having a close fit plunger die assembly (Adapa et al., 2006) was used to study the compression characteristics of selected agricultural straw (Adapa et al., 2002). The cylindrical die was 135.3 mm long and 6.30±0.5 mm in diameter. Thermal compound (Wakefield Engineering Inc., Wakefield, MA, USA) was coated on the outer surface of the die prior to wrapping the outer surface with copper shim stock. A dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, IL, USA) was then wound evenly around the shim stock to provide the necessary heat. One type-T thermocouple, connected to the outer surface of the cylinder, was linked to a temperature controller to regulate the power input to the heater, thus allowing temperature control of the cylinder. Another type-T thermocouple was also connected

to the outer cylinder wall, allowed verification of the cylinder temperature via a digital thermocouple reader (Shaw 2008). The pellet die was fitted on a stainless steel base having a hole matching its outer diameter. This gave stability and allowed the plunger to move straight down with no lateral movement. The plunger was attached to the upper moving crosshead of the Instron Model 1011 testing machine (Instron Corp., Canton, MA, USA).

C.3.6 Compression Test and Energy Calculations

The compaction apparatus was used to make a single compact in one stroke of the plunger from ground straw samples. In order to simulate frictional heating during commercial pelleting operation, the compaction die was maintained at a temperature of 95±1^{o}C (Adapa et al., 2006 and Mani et al., 2006b). The mass of samples used for making compacts varied between 0.5 and 0.7 g. Compressive force was applied using the Instron Model 1011 testing machine fitted with a 5000 N load cell and a 6.25 mm diameter plunger. Four preset loads of 1000, 2000, 3000 and 4400 N corresponding to pressures of 31.6, 63.2, 94.7 and 138.9 MPa, were used to compress samples in the die. The crosshead speed of the Instron testing machine was set at 50 mm min^{-1}. After compression, the plunger was retained in place for 30 s once the preset load was attained in order to avoid spring-back effect of biomass grinds (Adapa et al., 2006 and Mani et al., 2006b). Later, the base plate was removed and the compact was ejected out of the die by using the plunger. The mass, length and diameter of compacts were measured to determine the density in kg m^{-3}, following the extrusion of the compact. Ten replicates (pellets) were made using each ground straw samples. The durability represents the measure of shear and impact forces that a pellet could withstand during handling, storing and transportation process. The best possible method to measure compact durability is to use a dural pellet tester (Developed by the Bioprocessing Lab, Department of Agricultural and Bioresource Engineering, University of Saskatchewan, Canada) (Larsen et al. 1996). The method states that a 100 g of pellet samples are required to get appropriate results. Therefore, it is not feasible to perform this test using 10 pellets (~6 g).

During compression and extrusion process of individual compacts, the force-displacement data were recorded. Specific compression and extrusion energies were calculated following the methodology of Adapa et al. (2007b) and Mani et al. (2006a). The area under the force-displacement curve was integrated using the trapezoid rule (Cheney and Kincaid, 1980); when

combined with the pellet mass, it yielded the specific energy values in MJ/t. The specific energy calculations did not include the energy required to operate the Instron testing machine.

In this study the compacts are prepared by densifying material against a base plate (representing the specific energy required to overcome friction within the straw grinds) as opposed to commercial operation where compacts are formed due to back-pressure effect in the die. However, we have included the specific energy required to extrude the compact, which will closely emulate the specific energy required to overcome the friction between the ground straw and die.

C.3.7 Statistical Analysis

The experiments were set up as completely random experimental design with 10 replications of compacts and two-variable (straw and pressure) factorial design. Density was the dependent variable, while pressure was the independent variable. Statistical analyses were conducted using SAS for Windows (version 8.2) (SAS Institute, 1999). In order to further understand and explain the experimental variables and their interactions, the SAS general linear model (GLM) for completely randomized design (CRD) procedure was used and the Student-Neuman-Keuls test (SNK) was performed. SNK determines the difference between any two treatment means at 5% level of significance (SAS Manual, SAS Institute, 1999). Best predictor equations were developed with the highest coefficient of determination (R^2) with pressure being the independent variable. The equation parameters were estimated using MS Excel software and SAS software for Windows (version 8.2) (SAS Institute, 1999). Possible outliers were identified using the studentised residual method (Lund, 1975) and subsequently removed from further analysis.

C.4 Results and Discussion

The geometric mean particle diameter, bulk and particle densities of ground barley, canola, oat and wheat straw at 10% moisture content (wb) are listed in Table C.1. Figure C.1 shows that the grind particles were normally distributed for all four straw samples. Similar observation was reported by Mani et al. (2004b) for wheat and barley straw. The SNK test indicated that the geometric mean particle size of oat straw (0.347 mm) was significantly different ($P < 0.05$) than other straw samples. The mean bulk density of ground canola straw was highest (273 kg m^{-3});

however, the bulk densities for all the straw samples were not statistically different ($P > 0.05$). It was observed that ground wheat and barley straw have the highest (1585 kg/m^3) and lowest (1484 kg/m^3) mean particle densities, respectively. The mean particle density of barley, canola and oat straw were statistically similar, while the mean particle densities of canola, oat and wheat straw were not significantly different.

Table C.1: Geometric mean particle diameter, bulk and particles densities for four ground agricultural straw samples at 10% moisture content (wb).

Biomass	Geometric Mean Particle Diameter (mm)	Bulk density (kg m^{-3})	Particle density (kg m^{-3})
Barley Straw	0.384 ± 0.003 a γ†‡	261 ± 02 a	1484 ± 03 a
Canola Straw	0.391 ± 0.017 a	273 ± 11 a	1551 ± 47 ab
Oat Straw	0.347 ± 0.003 b	268 ± 04 a	1523 ± 15 ab
Wheat Straw	0.398 ± 0.006 a	269 ± 09 a	1585 ± 46 b

γ3 replicates; †95% confidence interval; ‡ Student-Neuman-Keuls test at 5% level of significance

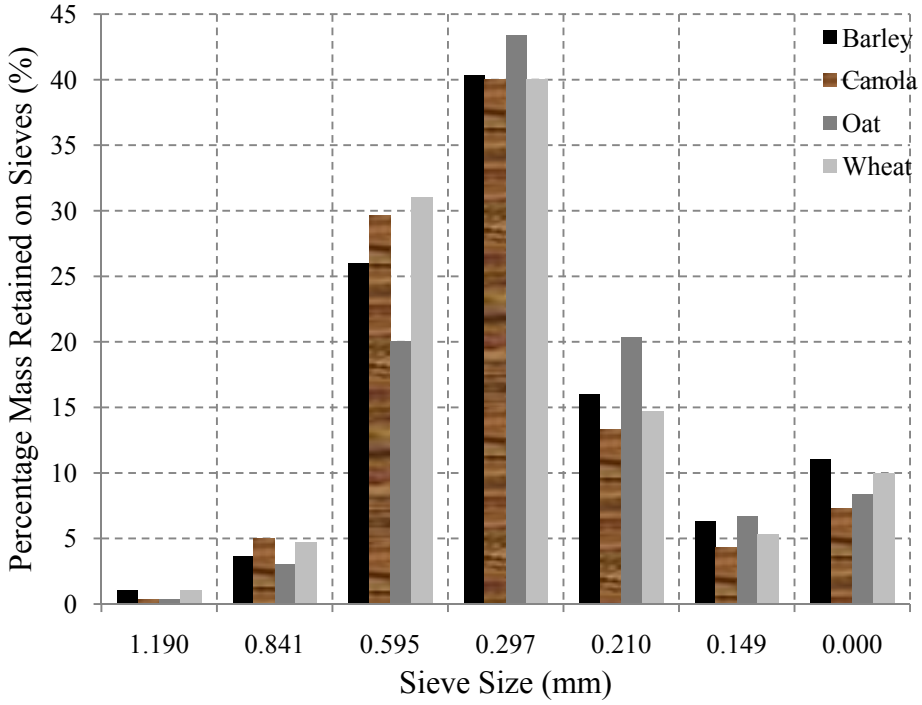


Figure C.1: Partical size distribution of barley, canola, oat and wheat straw grinds at grinder screen size of 1.98 mm

Table C.2 shows the average chemical composition of barley, canola, oat and wheat straw samples for tests performed in duplicates. Among the tested samples, canola straw had the highest protein content (6.53%); barley straw had the highest level of fat (1.91%) and lignin (17.13%), while wheat straw showed the highest levels of starch (2.58%) and ash (2.36%) contents. Canola and wheat straw showed highest level of cellulose (42.39%) and hemicelluloses (23.68%), respectively. Among the chemical components, the protein, starch and lignin may enhance the compact-ability of ground biomass (Mani et al., 2006b; Kaliyan and Morey, 2006a). Table C.2 also shows that the percentage of starch was significantly lower when compared to protein and lignin compounds in the four straw samples, except for wheat straw. Therefore, protein and lignin could be the deciding factors to enhance the binding characteristics of densified pellets. Protein plasticises under heat and acts as a binder, in turn increasing the strength of pelletised product (Winowiski, 1988; Briggs et al., 1999). In the presence of heat and moisture, gelatinization of starch occurs, which results in binding of ground biomass (Wood, 1987; Thomas et al., 1998). In addition, mechanical shearing during densification process also improves starch gelatinization (Kaliyan and Morey, 2006a) in the presence of moisture. At high elevated temperatures and pressures, lignin softens and helps the binding process. Lignin has thermosetting properties and a low melting point of about 140^{o}C (van Dam et al., 2004).

Table C.2: Chemical composition of selected agricultural straw samples.

Composition (% DM[a])	Barley Straw	Canola Straw	Oat Straw	Wheat Straw
Protein	3.62	6.53	5.34	2.33
Fat	1.91	0.69	1.65	1.59
Starch	0.11	0.34	0.12	2.58
Lignin	17.13	14.15	12.85	13.88
Cellulose[b]	33.25	42.39	37.60	34.20
Hemicellulose[c]	20.36	16.41	23.34	23.68
Ash	2.18	2.10	2.19	2.36

[a]DM – Dry Matter
[b]Cellulose percentage is calculated indirectly from percentage acid detergent fiber (ADF) and lignin (%ADF-%lignin) (Mani et al., 2006b).
[c]Hemicellulose percentage is calculated indirectly from percentage neutral detergent fiber (NDF) and ADF (%NDF-%ADF) (Mani et al., 2006b)

Figure C.2 shows a photograph of compacts manufactured using ground barley, canola, oat and wheat straw and four preset loads/pressures.

Figure C.2: Compacts manufactured using four agricultural straw samples at four preset loads / pressures

Table C.3 shows the effect of applied pressure on compact density and specific energy required for compression and extrusion of pellets from the four ground agricultural straws. The actual compressive force recorded by the Instron machine was slightly higher than the preset values (applied load). The recorded compressive forces had higher variability at higher preset loads due to the inertia of crosshead and limitations in testing machine control. Two SNK analyses were performed on the collected data. In the first SNK analysis, treatment means for the same straw sample at different pressures were compared and the differences were shown by designations of the lower case letters a, b and c. The second SNK analysis was performed to determine the

difference in treatment means for the four straw samples at the same pressure with the upper case letters D and E used to show the difference.

Table C.3: Effect of compressive forces (pressures) on compact density and specific energy required for compression and extrusion of agricultural straw compacts.

Biomass	Applied Load (N)	Compressive Force (N)	Pressure (MPa)	Compact Density (kg/m^3)	Specific Energy ($MJ\ t^{-1}$)	
					Compression	Total[¥]
Barley Straw	1000	1224 ± 42[*†]	30.5 ± 0.2	907 ± 31 aD	3.38 ± 0.25 aD[‡]	3.69 ± 0.28 aD
	2000	2339 ± 53	60.6 ± 0.3	978 ± 14 bD	5.42 ± 0.33 bD	5.81 ± 0.36 bD
	3000	3395 ± 50	91.2 ± 0.3	988 ± 26 bD	6.78 ± 0.93 cD	7.22 ± 1.01 cD
	4400	4725 ± 63	133.8 ± 0.6	977 ± 38 bD	8.77 ± 0.37 dD	9.29 ± 0.39 dD
Canola Straw	1000	1214 ± 41	30.2 ± 0.3	823 ± 73 aE	3.20 ± 0.72 aD	3.31 ± 0.82 aD
	2000	2324 ± 36	60.9 ± 0.3	934 ± 21 bE	5.25 ± 0.85 bD	5.42 ± 0.87 bD
	3000	3381 ± 42	90.9 ± 0.4	980 ± 17 cD	6.91 ± 0.25 cD	7.26 ± 0.30 cD
	4400	4569 ± 31	133.7 ± 0.4	1003 ± 21 cD	9.03 ± 0.32 dD	9.44 ± 0.33 dD
Oat Straw	1000	1211 ± 57	30.2 ± 0.2	849 ± 22 aE	4.58 ± 0.33 aE	5.25 ± 0.42 aE
	2000	2364 ± 33	60.5 ± 0.3	937 ± 56 bE	6.06 ± 0.26 bD	6.59 ± 0.27 bE
	3000	3438 ± 51	91.4 ± 0.3	991 ± 63 cD	7.09 ± 0.43 cD	7.62 ± 0.49 cD
	4400	4625 ± 21	133.7 ± 0.6	1011 ± 54 cD	8.94 ± 0.79 dD	9.57 ± 0.83 dD
Wheat Straw	1000	1210 ± 49	30.3 ± 0.4	813 ± 55 aE	3.33 ± 0.41 aD	3.59 ± 0.44 aD
	2000	2383 ± 50	60.7 ± 0.4	929 ± 30 bE	5.28 ± 0.98 bD	5.53 ± 0.98 bD
	3000	3333 ± 90	91.1 ± 0.4	931 ± 34 bE	6.17 ± 0.51 cE	6.39 ± 0.53 cE
	4400	4687 ± 41	133.4 ± 0.4	924 ± 23 bE	6.90 ± 0.39 dE	7.16 ± 0.40 dE

*10 replicates; † 95% confidence interval; ‡ Student-Neuman-Keuls test at 5% level of significance for same sample biomass at various applied load levels (a, b, and c); at same applied load for different sample biomass (D and E); ¥ Total Specific Energy = Specific Energy for Compression + Specific Energy for Extrusion.

C.4.1 Compact Density

Figure C.3 shows that the compact density for all four agricultural straw samples increased with an increase in pressure. The mean densities of barley, canola, oat and wheat straw compacts increased from 907 to 988 kg/m^3, 823 to 1003 kg/m^3, 849 to 1011 kg/m^3 and 813 to 924 kg/m^3, respectively, upon application of pressure in the range of 31.6 to 138.9 MPa. For barley and wheat straw pellets, the increase in density was significant ($P < 0.05$) for an increase of pressure from 31.6 to 63.2 MPa (Table C.3). Table C.3 also indicates that for canola and oat straw compacts, the increase in density were significant ($P < 0.05$) for an increase in applied pressure from 31.6 to 94.7 MPa. Application of higher pressures (> 94.7 MPa) did not affect the compact density as the compacts approached their respective particle densities. The wheat straw

compacts reached to their maximum density at a pressure of 63.2 MPa even though it has larger geometric mean particle diameter and particle densities (Table C.1). This could possibly be attributed to the lower total protein and lignin contents as compared to other straw material.

At pressures of 31.6 and 63.2 MPa, the density of compact from barley straw was significantly higher than the densities of other agricultural straw compacts (Table C.3), which could be attributed to a combination of lowest particle density (1484 kg/m^3) and geometric mean particles diameter. However, at pressures of 94.7 and 138.9 MPa, the density of compacts from wheat straw was significantly lower than the densities of other agricultural straw compacts. This could be due to the fact that wheat straw has both highest particles density (1585 kg/m^3) and geometric mean particle diameter.

Generally, at any particular pressure, the density of compacts was highest for oat straw followed by barley, canola and wheat straw in decreasing order (Figure C.3). This could be attributed to the geometric mean particle diameter for oat straw (0.347 mm), which was followed by barley (0.384 mm), canola (0.391 mm) and wheat (0.398 mm) straw in increasing order. The finer grind size has been reported to produce denser compacts (Kaliyan and Morey, 2006a and 2006b; Mani et al., 2002 and 2004a). Best predictor equations were developed to calculate the density of compacts manufactured from ground agricultural straw at various pressures after identifying and removing potential outliers (Figure C.3). One outlier for canola (31.6 MPa: 690 kg/m^3), one for oat (63.2 MPa: 812 kg/m^3), and one for wheat (31.6 MPa: 693 kg/m^3) were detected, which in turn improved their respective coefficient of determination (R^2). The resulting R^2 for barley, canola, oat and wheat straw were 0.56, 0.79, 0.67 and 0.62, respectively (Figure C.3) for best fit polynomial equations.

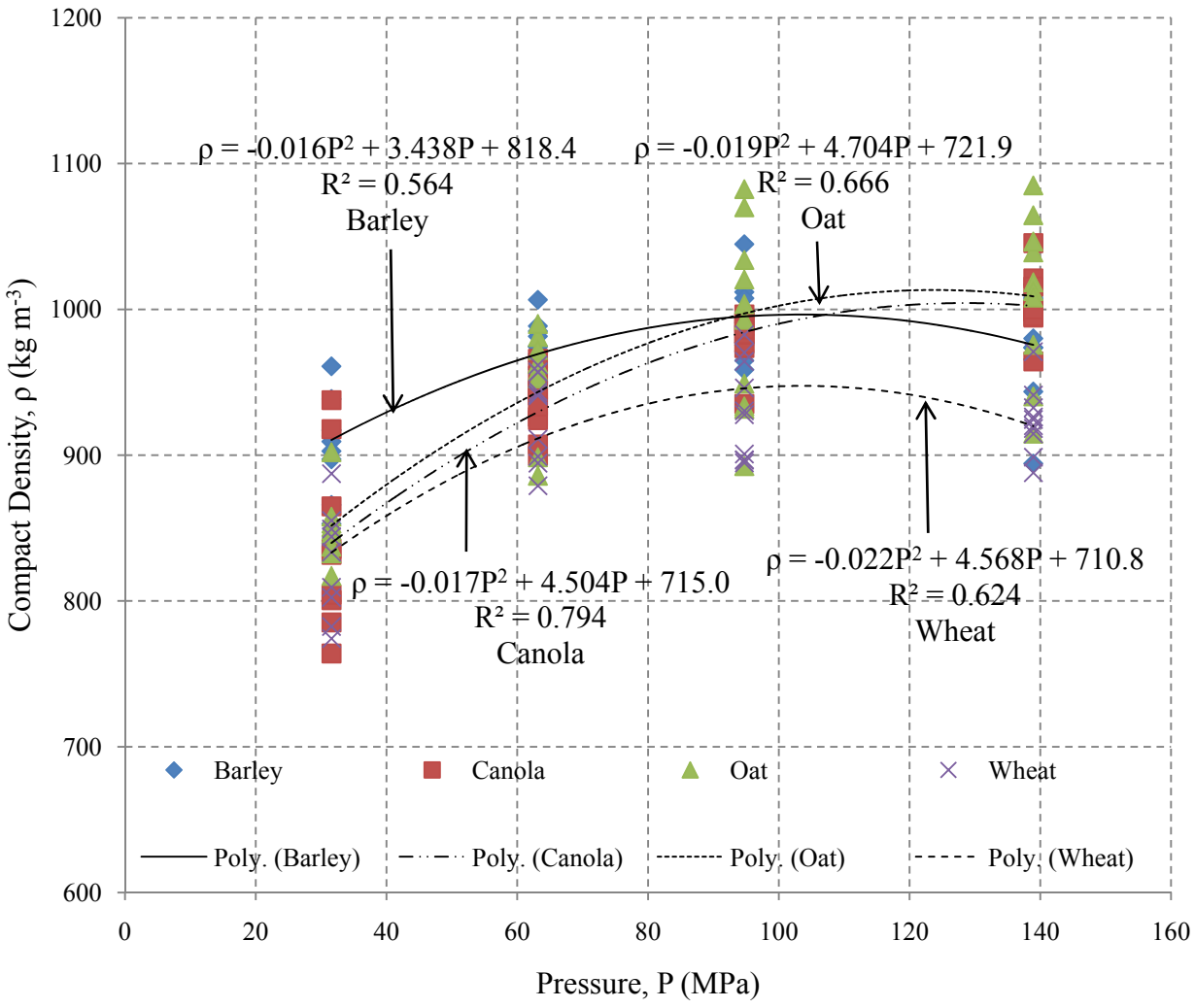


Figure C.3: Density of compacts and their respective predictive equations for four agricultural straw samples at four pressure levels. ρ is compact density (kg/m^3) and P is applied pressure (MPa).

C.4.2 Specific Energy

Table C.3 shows the total specific energy (MJ/t) of forming a compact, which is obtained from the summation of specific energy required from compression and extrusion of a compact. For all four agricultural straw samples, the total specific energy significantly increased ($P < 0.05$) with an increase in pressure from 31.6 to 138.9 MPa. For densifying barley, canola, oat and wheat straw, the mean total specific energy increased from 3.69 to 9.29 MJ/t, 3.31 to 9.44 MJ/t, 5.25 to 9.57 MJ/t, and 3.59 to 7.16 MJ/t, respectively. Even though, the total specific energy increased

significantly with pressure, the compact density of barley and wheat did not increase above a pressure of 63.2 MPa. Similarly, the compact density for canola and oat did not change above a pressure of 94.7 MPa. Therefore, a pressure of 63.2 MPa for barley and wheat straw, and a pressure of 94.7 MPa for canola and oat straw produced the highest density compacts with minimal specific energy consumption values.

At lower pressures of 31.6 and 63.2 MPa, densifying oat straw consumed significantly higher ($P < 0.05$) total specific energy as compared to densifying barley, canola and wheat straw. This could be due to the fact that the bulk densities for all four straw samples were statistically not different ($P > 0.05$); however, the geometric mean particle diameter of ground oat straw was significantly smaller than the other three ground samples (Table C.1). This resulted in larger plunger displacement values and consequently, higher specific energy values. At higher pressures of 94.7 and 138.9 MPa, densifying ground wheat straw consumed significantly lower total specific energy compared to other three straw samples (Table C.3), as a result of lower compact density values (Figure C.3).

It has been observed from Table C.3 that the percentage of specific energy required for extruding the pellet out of the die to form barley, canola, oat and wheat straw compacts varied between 6-9%, 3-4%, 7-13% and 4-7%, respectively. It has been observed that the percentage of specific extrusion energy values were higher at lower pressure values. Also, it was observed that the specific extrusion energy values increased with pressure, possibly due to the increase in radial pressure exerted by the compact. It has been observed that the highest extrusion values were obtained for oat having smallest geometric mean particle diameter (Table C.1), followed by barley and wheat in decreasing order. Canola straw did not follow the pattern and showed some variability in results. The percentage extrusion values reported in this study are higher than the values reported by Shaw (2008) for wheat and poplar biomass, while significantly lower than those reported by Mani et al. (2006a) for corn stover; Mewes (1959) and Bellinger and McColly (1961) for hay.

In general, at any particular pressure, the total specific energy for densifying the ground straw into compacts was highest for oat straw followed by barley, canola and wheat straw in decreasing order (Figure C.4). The variation in total specific energy has shown similar trend when compared to density (Figure C.4), which is evident as higher compaction of grinds will

demand higher specific energy values. Best predictor equations were developed to calculate the total specific energy required to manufacture compacts from ground agricultural straw at various pressures after identifying and removing potential outliers (Figure C.4). One outlier for barley (94.7 MPa: 9.1 MJ/t), two for canola (31.6 MPa: 5.3 MJ/t; 63.2 MPa: 7.2 MJ/t), and one for wheat straw (63.2 MPa: 8.2 MJ/t) were detected, which in turn improved their respective coefficient of determination (R^2). The resulting R^2 for barley, canola, oat and wheat straw were 0.94, 0.96, 0.90 and 0.92, respectively (Figure C.4).

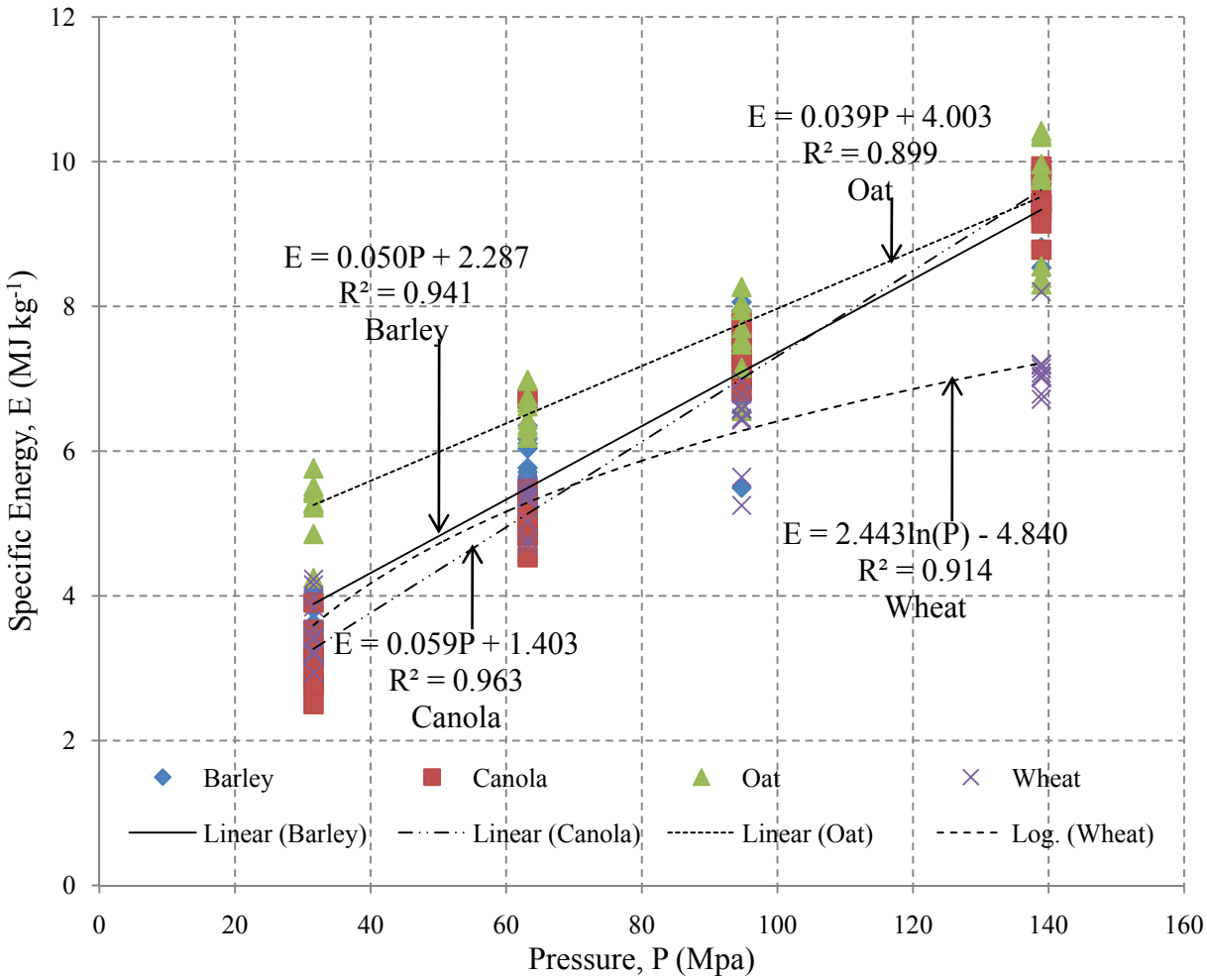


Figure C.4: Total specific energy required to form compacts and their respective predictive equations for four agricultural straw samples at four pressure levels. E is total specific energy (MJ/t) and P is applied pressure (MPa).

C.5 Conclusion

The densification of barley, canola, oat and wheat straw was investigated using four pressure levels. It was observed that a pressure of 63.2 MPa for barley and wheat, and a pressure level of 94.7 MPa for canola and oat produced highest density compacts with minimal specific energy consumption values. Best predictor equations were developed to predict compact density and the total specific energy required to manufacture compacts from four ground agricultural straw samples with highest coefficient of determination. The resulting R^2 for pellet density from barley, canola, oat and wheat straw were 0.77, 0.90, 0.87 and 0.73, respectively, and for total specific energy values were 0.96, 0.98, 0.96 and 0.92, respectively.